Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Copper-Catalyzed Aminothiolation of Terminal Alkynes with Tunable Regioselectivity

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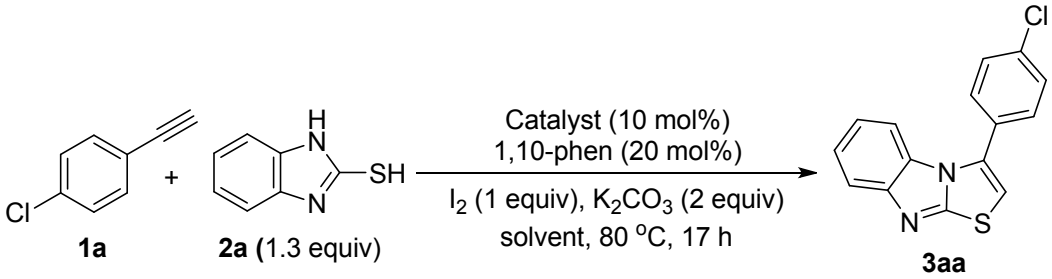
General Information

All commercially available reagents were used without further purification. Analytical TLC was performed on glass-backed plates pre-coated with silica gel, which were visualized by UV fluorescence (λmax = 254 nm) and/or by staining with 1% *w*/*v* $KMnO_4$ in 0.5 M aqueous K_2CO_3. ^1H NMR and ^{13}C NMR spectra were measured on a 500 MHz spectrometer (^1H: 500 MHz, ^{13}C: 125 MHz), using $CDCl_3$ or d^6-DMSO as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. All ^1H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm ($CHCl_3$). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.0 ppm) and were obtained with ^1H-decoupling. Data for ^1H NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sep, septet; m, multiplet; br, broad signal), coupling constant (Hz), integration. Data for ^{13}C NMR are described in terms of chemical shift (δ in ppm). High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. Melting points were measured on X4 melting point apparatus and uncorrected.

1-(Prop-2-ynyl)-1*H*-indole **1w**,[1] ligand 2,9-diisopropyl-1,10-phenanthroline (**L-2**),[2] and 2-[(*E*)-1,2-diiodoethenyl] pyridine (**1n'**)[3] were prepared according to the reported procedures.

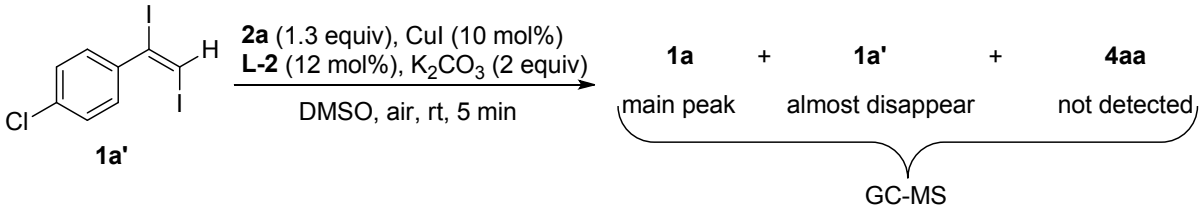
Table S1. Optimization of reaction conditions.[a]



Entry	Solvent	Catalyst	Yield of **3aa** (%)[b]
1	**CH_3CN**	CuI	**83**
2[c]	CH_3CN	CuI	64
3	EtOH	CuI	79
4	MeOH	CuI	75
5	*i*-PrOH	CuI	56
6	THF	CuI	33
7	1,4-dioxane	CuI	26
8	DME	CuI	35
9[d]	DMSO	CuI	24
10[d]	CH_3CN	CuBr	59
11[d]	CH_3CN	CuCl	55
12[d]	CH_3CN	CuCN	42
13[d]	CH_3CN	$CuBr_2$	51
14[d]	CH_3CN	$Cu(OTf)_2$	47
15[e]	CH_3CN	CuI	75

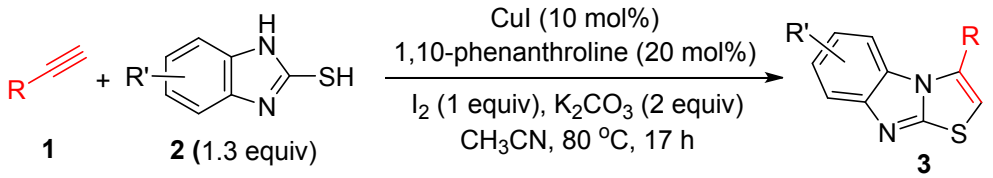
[a] Reaction conditions: 1a (0.2 mmol), **2a** (0.26 mmol), catalyst (0.02 mmol), ligand **L-1** (0.04 mmol), I_2 (0.2 mmol), K_2CO_3 (0.4 mmol), solvent (1 mL) under air at 80 °C for 17 h. [b] Isolated yield after column chromatography. [c] The reaction was run at 90 °C using 0.2 mmol of **2a**. [d] 0.20 mmol of **2a** (1.0 equiv) was used. [e] 0.28 mmol of **2a** (1.4 equiv) was used.

Control experiment



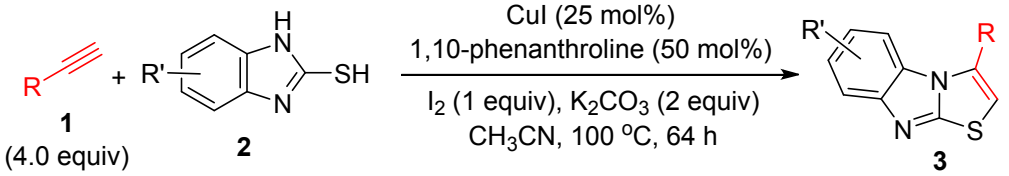
The reaction was run at rt for 5 min and then GC-MS of the reaction mixture was checked. The peak of starting material **1a'** almost disappeared and new big peak of alkyne **1a** appeared, while product **4aa** was not detected. It seems that under the above conditions the conversion of 1,2-diiodoalkene **1a'** to alkyne **1a** was much faster than the reaction of **1a'** with **2a** affording **4aa**.

General Procedure A for the synthesis of 3-substituted thiazolo[3, 2-a]benzimidazoles 3 (GP-A)



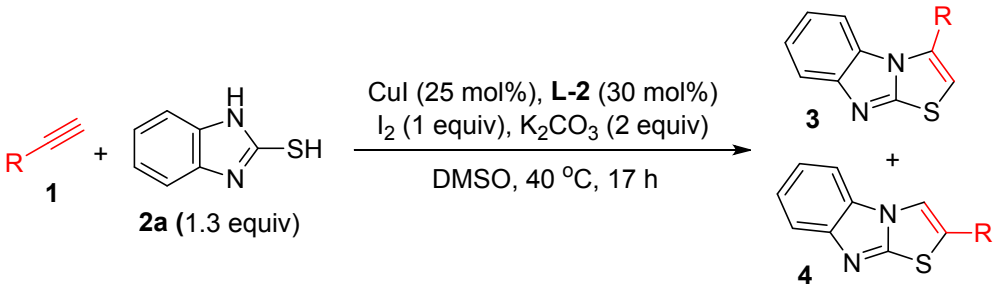
To a Schlenk tube (10 mL) were added I_2 (0.2 mmol), K_2CO_3 (0.4 mmol), **2** (0.26 mmol), CuI (0.02 mmol), 1,10-phen (**L-1**) (0.04 mmol), alkyne **1** (0.2 mmol), and 1 mL of CH_3CN sequentially under air and then the resulting mixture was stirred at room temperature for 2 min. The tube was then sealed and the reaction mixture was stirred at 80 °C for 17 h. After cooling to room temperature, the mixture was filtered through Celite and the filtrate was concentrated. The crude mixture was purified by flash column chromatography on silica gel.

General Procedure B for the synthesis of 3-substituted thiazolo[3, 2-a]benzimidazoles 3 (GP-B)



To a Schlenk tube (10 mL) were added I_2 (0.2 mmol), K_2CO_3 (0.4 mmol), **2** (0.20 mmol), CuI (0.05 mmol), 1,10-phen (**L-1**) (0.10 mmol), alkyne **1** (0.8 mmol), and 1 mL of CH_3CN sequentially under air and then the resulting mixture was stirred at room temperature for 2 min. The tube was then sealed and the reaction mixture was stirred at 100 °C for 64 h. After cooling to room temperature, the mixture was filtered through Celite and the filtrate was concentrated. The crude mixture was purified by flash column chromatography on silica gel.

General Procedure C for the synthesis of 2-substituted thiazolo[3, 2-a]benzimidazoles 4 (GP-C)

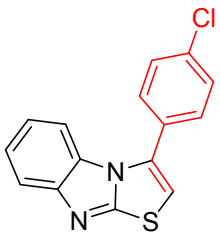


To a Schlenk tube (10 mL) were added **2a** (0.26 mmol), I_2 (0.2 mmol), K_2CO_3 (0.4 mmol), CuI (0.05 mmol), 2,9-diisopropyl-1,10-phenanthroline (**L-2**) (0.06 mmol), alkyne **1** (0.2 mmol), and 1 mL of DMSO sequentially under air and then the resulting

mixture was stirred at room temperature for 2 min. The tube was then sealed and the reaction mixture was stirred at 40 ^{o}C for 17 h. After cooling to room temperature, the reaction mixture was diluted with EA (20 mL), washed with water (10 mL) and brine (2 x 10 mL), dried over anhydrous Na_2SO_4. Filtration, concentration, and purification by flash column chromatography on silica gel afforded the desired products **4**.

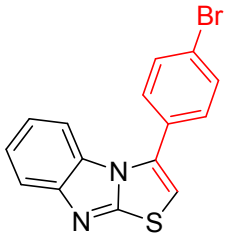
Syntheses and characterization of 3-substituted thiazolo[3, 2-a]benzimidazoles (3)

3-(4-Chlorophenyl)thiazolo[3,2-a]benzimidazole (3aa)[4]



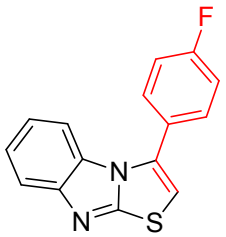
The reaction was performed following **GP-A** with CuI (3.7 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.3 mg, 0.04 mmol), I_2 (51.6 mg, 0.20 mmol), K_2CO_3 (54.5 mg, 0.39 mmol), 4-chlorophenylacetylene (27.8 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.3 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (47.9 mg, 83%). Mp 198–199 °C. (lit. Mp 199−201 °C).
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 8.0 Hz, 1 H), 7.20 (d, *J* = 8.5 Hz, 1 H), 7.08 (t, *J* = 8.0 Hz, 1 H), 6.60 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.0, 148.7, 136.3, 132.9, 130.0, 129.9, 129.3, 127.8, 123.4, 120.5, 119.3, 111.4, 107.7.

3-(4-Bromophenyl)thiazolo[3,2-a]benzimidazole (3ba)[4]



The reaction was performed following **GP-A** with CuI (3.7 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.6 mg, 0.04 mmol), I_2 (50.5 mg, 0.20 mmol), K_2CO_3 (56.0 mg, 0.41 mmol), 4-bromophenylacetylene (36.3 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.3 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (43.2 mg, 65%). Mp 198–199 °C. (lit. Mp 205−206 °C).
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 1 H), 7.71 (d, *J* = 8.5 Hz, 2 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 1 H), 7.08 (t, *J* = 7.8 Hz, 1 H), 6.61 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.0, 148.7, 133.0, 132.2, 130.2, 129.9, 128.2, 124.5, 123.5, 120.5, 119.3, 111.4, 107.7.

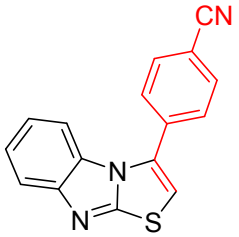
3-(4-Fluorophenyl)thiazolo[3,2-a]benzimidazole (3ca)[5,6]



The reaction was performed following **GP-A** with CuI (3.7 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.3 mg, 0.04 mmol), I_2 (50.6 mg, 0.20 mmol), K_2CO_3 (55.8 mg, 0.41 mmol), 4-fluorophenylacetylene (24.1 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.7 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (46.0 mg, 85%). Mp 159–160 °C (lit.[5] Mp 145−147 °C; lit.[6] Mp 174−177°C).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1 H), 7.64 (dd, *J* = 7.5, 5.5 Hz, 2 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 7.27 (t, *J* = 8.3 Hz, 2 H), 7.17 (d, *J* = 8.5 Hz, 1 H), 7.08 (t, *J* = 7.8 Hz, 1 H), 6.59 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 163.7 (d, *J* = 250.9 Hz), 157.0, 148.7, 133.1, 130.9 (d, *J* = 7.7 Hz), 130.0, 125.5 (d, *J* = 4.0 Hz), 123.4, 120.5, 119.3, 116.2 (d, *J* = 22.4 Hz), 111.4, 107.4.

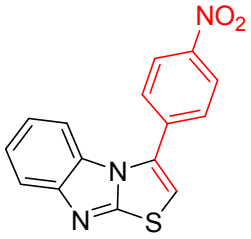
3-(4-Cyanophenyl)thiazolo[3,2-a]benzimidazole (3da)



The reaction was performed following **GP-A** with CuI (3.7 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.1 mg, 0.04 mmol), I_2 (51.5 mg, 0.20 mmol), K_2CO_3 (55.7 mg, 0.40 mmol), 4-ethynylbenzonitrile (25.6 mg, 0.20 mmol), 2-mercaptobenzimidazole (38.7 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1 to 1/1) to afford the title compound as a yellow solid (42.2 mg, 76%). Mp 249–252 °C.

^{1}H NMR (500.13 MHz, d_6-DMSO) δ 8.12 (d, *J* = 8.0 Hz, 2 H), 7.99 (d, *J* = 8.5 Hz, 2 H), 7.73 (d, *J* = 8.0 Hz, 1 H), 7.42 (s, 1 H), 7.34 (t, *J* = 7.3 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 1 H), 7.14 (t, *J* = 7.5 Hz, 1 H); **^{13}C NMR (125.76 MHz, DMSO-*d_6*)** δ 156.6, 148.2, 133.4, 133.0, 131.8, 129.6, 123.2, 120.6, 118.8, 118.4, 112.6, 111.6, 110.0; **HRMS** calcd for $C_{16}H_{10}N_3S$ $[M+H]^+$: 276.0590. Found: 276.0586.

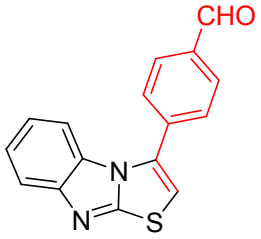
3-(4-Nitrophenyl)thiazolo[3,2-a]benzimidazole (3ea)[4]



The reaction was performed following **GP-A** with CuI (3.9 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.4 mg, 0.04 mmol), I_2 (51.2 mg, 0.20 mmol), K_2CO_3 (56.0 mg, 0.41 mmol), 1-ethynyl-4-nitrobenzene (29.0 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.3 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1 to 1/1) to afford the title compound as a yellow solid (31.5 mg, 54%). Mp 256–258 °C. (lit. Mp 258−260 °C).

^{1}H NMR (500.13 MHz, DMSO-d_6) δ 8.47 (d, *J* = 8.5 Hz, 2 H), 8.07 (d, *J* = 8.5 Hz, 2 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.48 (s, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.26 (d, *J* = 8.0 Hz, 1 H), 7.15 (t, *J* = 7.8 Hz, 1 H); **^{13}C NMR (125.76 MHz, DMSO-d_6)** δ 156.6, 148.2, 135.1, 131.5, 130.0, 129.6, 124.2, 123.3, 120.6, 118.9, 111.7, 111.5.

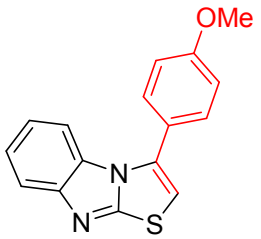
3-(4-Formylphenyl)thiazolo[3,2-a]benzimidazole (3fa)



The reaction was performed following **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.3 mg, 0.04 mmol), I_2 (50.5 mg, 0.20 mmol), K_2CO_3 (55.6 mg, 0.40 mmol), 4-ethynylbenzaldehyde (25.7 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.1 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1) to afford the title compound as a yellow solid (34.0 mg, 62%). Mp 185–186 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 10.14 (s, 1 H), 8.08 (d, *J* = 8.0 Hz, 2 H), 7.85 (d, *J* = 8.0 Hz, 2 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.34 (t, *J* = 7.8 Hz, 1 H), 7.23 (d, *J* = 8.5 Hz, 1 H), 7.09 (t, *J* = 8.0 Hz, 1 H), 6.74 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 191.2, 157.1, 148.7, 137.2, 134.9, 133.0, 130.1, 129.9, 129.1, 123.6, 120.7, 119.5, 111.5, 109.1; **HRMS** calcd for $C_{16}H_{11}N_2OS$ $[M+H]^+$: 279.0587. Found: 279.0581.

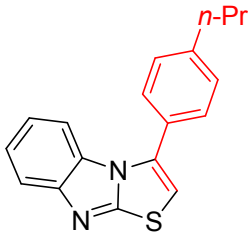
3-(4-Methoxyphenyl)thiazolo[3,2-a]benzimidazole (3ga)[4,5]



The reaction was performed following **GP-A** with CuI (3.9 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.3 mg, 0.04 mmol), I_2 (51.0 mg, 0.20 mmol), K_2CO_3 (55.8 mg, 0.40 mmol), 1-ethynyl-4-methoxybenzene (26.5 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.5 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (46.0 mg, 82%). Mp 149–150 °C. (lit. Mp 148−150 °C).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1 H), 7.55 (d, *J* = 8.5 Hz, 2 H), 7.30 (t, *J* = 7.8 Hz, 1 H), 7.23 (d, *J* = 8.5 Hz, 1 H), 7.08-7.00 (m, 3 H), 6.49 (s, 1 H), 3.91 (s, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 160.9, 157.1, 148.7, 134.0, 130.2, 130.1, 123.2, 121.5, 120.2, 119.1, 114.3, 111.6, 106.2, 55.4.

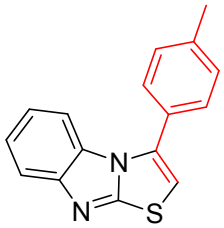
3-(4-Propylphenyl)thiazolo[3,2-a]benzimidazole (3ha)



The reaction was performed following **GP-A** with CuI (3.9 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.2 mg, 0.04 mmol), I_2 (50.4 mg, 0.20 mmol), K_2CO_3 (56.3 mg, 0.41 mmol), 1-ethynyl-4-propylbenzene (29.1 mg, 0.20 mmol), 2-mercaptobenzimidazole (38.9 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a colourless liquid (47.4 mg, 80%).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.5 Hz, 2 H), 7.31 (t, *J* = 7.5 Hz, 1 H), 7.25 (d, *J* = 8.0 Hz, 1 H), 7.05 (t, *J* = 7.5 Hz, 1 H), 6.53 (s, 1 H), 2.71 (t, *J* = 7.5 Hz, 2 H), 1.79-1.67 (m, 2 H), 1.01 (t, *J* = 7.5 Hz, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.2, 148.7, 145.0, 134.3, 130.1, 128.9, 128.6, 126.6, 123.2, 120.3, 119.1, 111.7, 106.6, 37.8, 24.3, 13.8; **HRMS** calcd for $C_{18}H_{17}N_2S$ $[M+H]^+$: 293.1107. Found: 293.1108.

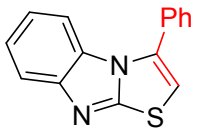
3-(4-Methylphenyl)thiazolo[3,2-a]benzimidazole (3ia)[4-6]



The reaction was performed following **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.2 mg, 0.04 mmol), I_2 (51.8 mg, 0.20 mmol), K_2CO_3 (55.4 mg, 0.40 mmol), 4-ethynyltoluene (23.5 mg, 0.20 mmol), 2-mercaptobenzimidazole (38.7 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (47.4 mg, 80%). Mp 120–122 °C. (lit.[4] Mp 118−121 °C).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1 H), 7.53 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 7.5 Hz, 2 H), 7.31 (t, *J* = 7.8 Hz, 1 H), 7.25 (d, *J* = 8.0 Hz, 1 H), 7.06 (t, *J* = 7.5 Hz, 1 H), 6.54 (s, 1 H), 2.49 (s, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.2, 148.7, 140.3, 134.3, 130.1, 129.6, 128.7, 126.5, 123.2, 120.3, 119.1, 111.7, 106.6, 21.4.

3-Phenylthiazolo[3,2-a]benzimidazole (3ja)[4-6]

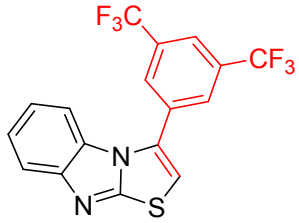


The reaction was performed following **GP-A** with CuI (4.0 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.6 mg, 0.04 mmol), I_2 (51.0 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40

mmol), phenylacetylene (21.9 μL, d = 0.93 g/mL, 20.4 mg, 0.20 mmol), 2-mercaptobenzimidazole (38.5 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound as a white solid (44.0 mg, 88%). Mp 137–138 °C. (lit.[4] Mp 138−140 °C).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1 H), 7.70-7.63 (m, 2 H), 7.61-7.52 (m, 3 H), 7.33 (t, *J* = 7.5 Hz, 1 H), 7.23 (d, *J* = 8.5 Hz, 1 H), 7.07 (t, *J* = 7.8 Hz, 1 H), 6.61 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.2, 148.7, 134.3, 130.12, 130.08, 129.4, 129.0, 128.8, 123.4, 120.4, 119.2, 111.7, 107.2.

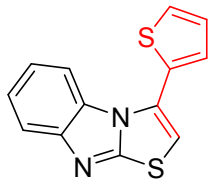
3-(3,5-Bis(trifluoromethyl)phenyl)thiazolo[3,2-a]benzimidazole (3ka)



The reaction was performed following **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.4 mg, 0.04 mmol), I_2 (50.5 mg, 0.20 mmol), K_2CO_3 (54.7 mg, 0.40 mmol), 1-ethynyl-3,5-bis(trifluoromethyl)benzene (35.4 μL, d = 1.346 g/mL, 47.6 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.1 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a yellow solid (62.1 mg, 80%). Mp 120–122 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.17 (s, 2 H), 8.11 (s, 1 H), 7.85 (d, *J* = 8.0 Hz, 1 H), 7.40 (t, *J* = 7.8 Hz, 1 H), 7.16 (t, *J* = 7.8 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 6.86 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.9, 148.8, 132.8 (q, *J* = 33.6 Hz), 131.6, 131.0, 129.8, 128.79, 128.77, 123.9, 123.7 (sep, *J* = 3.6 Hz), 122.8 (q, *J* = 273.1 Hz), 121.1, 119.8, 110.9, 110.3; **HRMS** calcd for $C_{17}H_9F_6N_2S$ $[M+H]^+$: 387.0385. Found: 387.0393.

3-Thiophen-2-ylthiazolo[3,2-a]benzimidazole (3la)[4, 5]

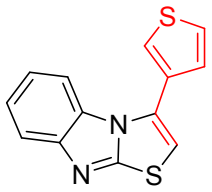


The reaction was performed following **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.5 mg, 0.04 mmol), I_2 (51.3 mg, 0.20 mmol), K_2CO_3 (55.6 mg, 0.40 mmol), 2-ethynylthiophene (21.6 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.4 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as a white solid (30.1 mg, 59%). Mp 94–95 °C. (lit.[4] Mp 94−95°C).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 1 H), 7.56 (d, *J* = 5.0 Hz, 1 H), 7.45 (d, *J* = 3.0 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.34 (t, *J* = 7.8 Hz, 1 H), 7.25 (t, *J*

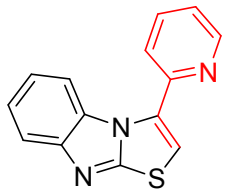
= 8.0 Hz, 1 H), 7.11 (t, *J* = 7.8 Hz, 1 H), 6.72 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.5, 148.5, 130.0, 129.5, 129.0, 128.1, 127.7, 127.0, 123.5, 120.6, 119.2, 111.5, 109.4.

3-Thiophen-2-ylthiazolo[3,2-a]benzimidazole (3ma)



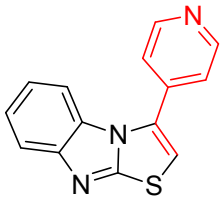
The reaction was performed following **GP-A** with CuI (3.9 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.4 mg, 0.04 mmol), I_2 (52.0 mg, 0.20 mmol), K_2CO_3 (55.1 mg, 0.40 mmol), 3-ethynylthiophene (21.1 mg, 0.20 mmol), 2-mercaptobenzimidazole (38.7 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (40.1 mg, 80%). Mp 144–147 °C.
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 1 H), 7.66 (t, *J* = 1.5 Hz, 1 H), 7.56 (dd, *J* = 4.5, 3.0 Hz, 1 H), 7.37 (dd, *J* = 5.0, 1.0 Hz, 1 H), 7.35-7.28 (m, 2 H), 7.10 (t, *J* = 7.8 Hz, 1 H), 6.62 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.8, 148.5, 130.0, 129.4, 129.3, 127.7, 127.0, 126.4, 123.4, 120.6, 119.1, 111.4, 107.4; **HRMS** calcd for $C_{13}H_9N_2S_2$ $[M+H]^+$: 257.0202. Found: 257.0204.

3-Pyridin-2-ylthiazolo[3,2-a]benzimidazole (3na)[4]



The reaction was performed following **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.3 mg, 0.04 mmol), I_2 (51.2 mg, 0.20 mmol), K_2CO_3 (55.5 mg, 0.40 mmol), 2-ethynylpyridine (21.5 mg, 0.21 mmol), 2-mercaptobenzimidazole (39.5 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1 to 1/1, with 0.5% Et_3N) to afford the title compound as a yellow solid (39.9 mg, 76%). Mp 163–165 °C. (lit. Mp 168−170 °C).
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.81 (d, *J* = 4.5 Hz, 1 H), 7.89-7.80 (m, 2 H), 7.77 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.42 (dd, *J* = 6.8, 5.3 Hz, 1 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 7.14 (t, *J* = 7.8 Hz, 1 H), 6.90 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.1, 149.5, 148.62, 148.58, 137.2, 134.5, 130.6, 124.2, 123.4, 122.9, 120.5, 118.9, 113.9, 110.1.

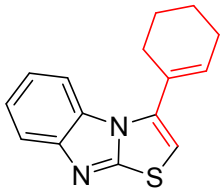
3-Pyridin-4-ylthiazolo[3,2-a]benzimidazole (3oa)



The reaction was performed following **GP-A** with CuI (3.9 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.2 mg, 0.04 mmol), I_2 (51.6 mg, 0.20 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), 4-ethynylpyridine (20.8 mg, 0.20 mmol), 2-mercaptobenzimidazole (38.8 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 1/2, with 0.5% Et_3N) to afford the title compound as a yellow solid (33.6 mg, 66%). Mp 144–147 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.85 (dd, *J* = 4.5, 1.5 Hz, 2 H), 7.81 (d, *J* = 8.5 Hz, 2 H), 7.60 (d, *J* = 4.5, 1.5 Hz, 2 H), 7.36 (t, *J* = 8.0 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 7.13 (t, *J* = 8.0 Hz, 1 H), 6.78 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.0, 150.7, 148.7, 137.1, 131.7, 129.8, 123.8, 122.6, 120.9, 119.6, 111.5, 110.0; **HRMS** calcd for $C_{14}H_{10}N_3S$ $[M+H]^+$: 252.0590. Found: 252.0599.

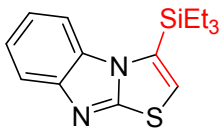
3-(Cyclohexen-1-yl)thiazolo[3,2-a]benzimidazole (3pa)



The reaction was performed following **GP-A** with CuI (3.9 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.5 mg, 0.04 mmol), I_2 (50.3 mg, 0.20 mmol), K_2CO_3 (56.0 mg, 0.41 mmol), 1-ethynylcyclohex-1-ene (21.8 mg, 0.21 mmol), 2-mercaptobenzimidazole (39.4 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (24.4 mg, 47%). Mp 154–155 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.0 Hz, 1 H), 7.60 (d, *J* = 8.5 Hz, 1 H), 7.34 (t, *J* = 7.8 Hz, 1 H), 7.20 (t, *J* = 7.8 Hz, 1 H), 6.40 (s, 1 H), 6.26-6.20 (m, 1 H), 2.43-2.35 (m, 2 H), 2.34-2.25 (m, 2 H), 1.93-1.86 (m, 2 H), 1.83-1.74 (m, 2 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.1, 148.6, 136.2, 132.4, 130.0, 127.6, 123.1, 120.5, 119.1, 111.3, 105.1, 28.2, 25.3, 22.4, 21.6; **HRMS** calcd for $C_{15}H_{15}N_2S$ $[M+H]^+$: 255.0951. Found: 255.0962.

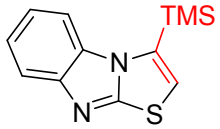
3-(Triethylsilyl)thiazolo[3,2-a]benzimidazole (3qa)



The reaction was performed following slightly modified **GP-A** with CuI (3.9 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.2 mg, 0.04 mmol), I_2 (50.5 mg, 0.20 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), 2-mercaptobenzimidazole (30.3 mg, 0.20 mmol), (triethylsilyl)acetylene (112.4 mg, 0.80 mmol), and 1 mL of CH_3CN at 80 °C. The

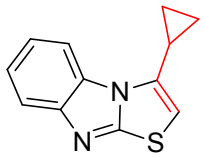
crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound as a colourless liquid (42.0 mg, 72%).
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.83-7.65 (m, 2 H), 7.29 (t, *J* = 6.8 Hz, 1 H), 7.19 (t, *J* = 7.5 Hz, 1 H), 6.77 (s, 1 H), 1.03-0.80 (m, 15 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 159.6, 148.7, 132.7, 130.7, 123.0, 120.6, 119.9, 119.4, 111.2, 7.2, 3.2; **HRMS** calcd for $C_{15}H_{21}N_2SSi$ $[M+H]^+$: 289.1190. Found: 289.1194.

3-(Trimethylsilyl)thiazolo[3,2-a]benzimidazole (3ra)



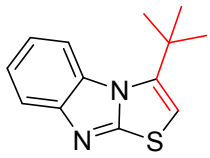
The reaction was performed following slightly modified **GP-A** with CuI (3.6 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.5 mg, 0.04 mmol), I_2 (52.4 mg, 0.21 mmol), K_2CO_3 (55.5 mg, 0.40 mmol), 2-mercaptobenzimidazole (30.3 mg, 0.20 mmol), (trimethylsilyl)acetylene (79.6 mg, 0.81 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound as a colourless liquid (30.4 mg, 61%).
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1 H), 7.69 (d, *J* = 8.0 Hz, 1 H), 7.29 (t, *J* = 8.0 Hz, 1 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 6.76 (s, 1 H), 0.45 (s, 9 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 159.5, 148.5, 135.4, 130.6, 123.0, 120.6, 119.3, 118.9, 111.4, -1.1; **HRMS** calcd for $C_{12}H_{15}N_2SSi$ $[M+H]^+$: 247.0720. Found: 247.0719.

3-(Cyclopropyl)thiazolo[3,2-a]benzimidazole (3sa)[6]



The reaction was performed following **GP-B** with CuI (9.4 mg, 0.05 mmol), 1,10-phen (**L-1**) (18.0 mg, 0.10 mmol), I_2 (50.2 mg, 0.20 mmol), K_2CO_3 (55.1 mg, 0.40 mmol), cyclopropylacetylene (67.8 μL, d = 0.78 g/mL, 52.9 mg, 0.80 mmol), 2-mercaptobenzimidazole (30.0 mg, 0.20 mmol), and 1 mL of CH_3CN at 100 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (28.9 mg, 68%). Mp 82–83 °C. (lit. Mp 101−103 °C).
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.5 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 7.25 (t, *J* = 7.8 Hz, 1 H), 6.30 (d, *J* = 1.5 Hz, 1 H), 2.24-2.15 (m, 1 H), 1.18-1.12 (m, 2 H), 0.91-0.83 (m, 2 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.9, 148.5, 135.8, 130.3, 123.2, 120.6, 119.0, 111.3, 104.5, 8.6, 6.1.

3-*tert*-Butylthiazolo[3,2-a]benzimidazole (3ta)[4,7]

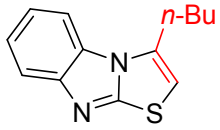


The reaction was performed following **GP-B** with CuI (9.7 mg, 0.05 mmol), 1,10-

phen (**L-1**) (17.9 mg, 0.10 mmol), I_2 (51.9 mg, 0.20 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), 3,3-dimethylbut-1-yne (98.5 μL, d = 0.667 g/mL, 65.7 mg, 0.80 mmol), 2-mercaptobenzimidazole (30.0 mg, 0.20 mmol), and 1 mL of CH_3CN at 100 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (28.0 mg, 61%). Mp 48–50 °C. (lit.[4] Mp 49−50 °C).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 7.27 (t, *J* = 7.8 Hz, 1 H), 6.40 (s, 1 H), 1.59 (s, 9 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 158.7, 148.8, 143.9, 130.1, 123.1, 120.4, 119.3, 114.0, 102.9, 33.5, 28.5.

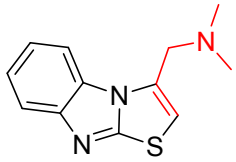
3-Butylthiazolo[3,2-a]benzimidazole (3ua)[4,6]



The reaction was performed following **GP-B** with CuI (9.2 mg, 0.05 mmol), 1,10-phen (**L-1**) (18.1 mg, 0.10 mmol), I_2 (51.2 mg, 0.20 mmol), K_2CO_3 (54.8 mg, 0.40 mmol), hex-1-yne (91.9 μL, d = 0.715 g/mL, 65.7 mg, 0.80 mmol), 2-mercaptobenzimidazole (30.3 mg, 0.20 mmol), and 1 mL of CH_3CN at 100 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (34.5 mg, 74%). Mp 86–88 °C. (lit.[4] Mp 85−87 °C).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 1 H), 7.71 (d, *J* = 8.0 Hz, 1 H), 7.35 (t, *J* = 7.8 Hz, 1 H), 7.24 (t, *J* = 7.5 Hz, 1 H), 6.31 (s, 1 H), 3.03 (t, *J* = 7.8 Hz, 1 H), 1.86-1.76 (m, 2 H), 1.58-1.49 (m, 2 H), 1.01 (t, *J* = 7.5 Hz, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.3, 148.5, 134.5, 130.1, 123.1, 120.6, 119.1, 110.8, 103.7, 28.8, 28.0, 22.2, 13.7.

***N,N*-Dimethylthiazolo[3,2-a]benzimidazol-3-yl-methanamine (3va)**

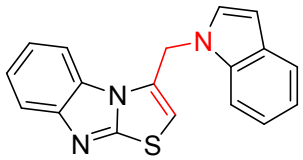


The reaction was performed following slightly modified **GP-A** with CuI (3.7 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.5 mg, 0.04 mmol), I_2 (50.6 mg, 0.20 mmol), K_2CO_3 (55.1 mg, 0.40 mmol), 1-dimethylamino-2-propyne (66.6 mg, 0.80 mmol), 2-mercaptobenzimidazole (30.4 mg, 0.20 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 1/1, with 0.5% Et_3N) to afford the title compound as a colourless liquid (27.4 mg, 59%).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 1 H), 7.34 (t, *J* = 7.8 Hz, 1 H), 7.24 (t, *J* = 7.5 Hz, 1 H), 6.56 (s, 1 H), 3.71 (s, 2 H), 2.34 (s, 6 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.2, 148.4, 131.8, 130.3, 123.3, 120.8, 118.8, 112.6, 107.7, 56.5, 45.0; **HRMS** calcd for $C_{12}H_{14}N_3S$ $[M+H]^+$: 232.0903.

Found: 232.0910.

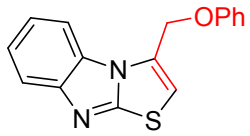
3-((1H-Indol-1-yl)methyl)thiazolo[3,2-a]benzimidazole (3wa)



The reaction was performed following **GP-A** with CuI (3.6 mg, 0.019 mmol), 1,10-phen (7.1 mg, 0.039 mmol), I_2 (51.9 mg, 0.20 mmol), K_2CO_3 (55.5 mg, 0.40 mmol), 1-(2-propyn-1-yl)-1*H*-indole (30.8 mg, 0.20 mmol), 2-mercaptobenzimidazole (38.4 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1, with 0.5% Et_3N) to afford the title compound as a white solid (22.5 mg, 37%). Mp 195–198 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.4 (d, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 7.5 Hz, 1 H), 7.48 (d, *J* = 7.8 Hz, 1 H), 7.35-7.25 (m, 2 H), 7.23-7.17 (m, 1 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 7.12 (d, *J* = 7.5 Hz, 1 H), 7.06 (d, *J* = 3.0 Hz, 1 H), 6.54 (d, *J* = 2.5 Hz, 1 H), 6.00 (s, 1 H), 5.64 (s, 2 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.2, 148.3, 136.1, 129.8, 129.4, 128.9, 127.3, 123.8, 122.6, 121.5, 121.3, 120.4, 119.5, 110.5, 109.1, 107.4, 103.4, 43.9; **HRMS** calcd for $C_{18}H_{14}N_3S$ $[M+H]^+$: 304.0903. Found: 304.0904.

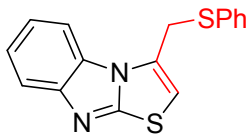
3-Phenoxymethylthiazolo[3,2-a]benzimidazole (3xa)



The reaction was performed following **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.3 mg, 0.04 mmol), I_2 (51.3 mg, 0.20 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), phenyl propargyl ether (26.7 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.6 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1) to afford the title compound as a white solid (50.0 mg, 88%). Mp 121–122 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.5 Hz, 1 H), 7.67 (d, *J* = 8.5 Hz, 1 H), 7.41-7.31 (m, 3 H), 7.20 (t, *J* = 7.8 Hz, 1 H), 7.07 (t, *J* = 7.5 Hz, 1 H), 7.01 (d, *J* = 8.5 Hz, 2 H), 6.79 (s, 1 H), 5.28 (s, 2 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.3, 156.8, 148.3, 129.9, 129.8, 129.0, 123.5, 122.2, 121.2, 119.1, 115.0, 111.6, 109.9, 62.3; **HRMS** calcd for $C_{16}H_{13}N_2OS$ $[M+H]^+$: 281.0743. Found: 281.0750.

3-Phenylthiomethylthiazolo[3,2-a]benzimidazole (3ya)

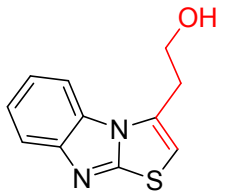


The reaction was performed following **GP-A** with CuI (4.0 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.5 mg, 0.04 mmol), I_2 (51.0 mg, 0.20 mmol), K_2CO_3 (55.6 mg, 0.40 mmol), phenyl propargyl sulfide (29.4 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.1 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified

by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a liquid (37.2 mg, 63%). Mp 121–123 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.5 Hz, 1 H), 7.38 (t, *J* = 7.8 Hz, 1 H), 7.31-7.24 (m, 6 H), 6.23 (s, 1 H), 4.33 (s, 2 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.9, 148.4, 13.1, 132.4, 129.8, 129.5, 129.2, 128.1, 123.4, 120.9, 119.2, 111.5, 107.6, 32.7; **HRMS** calcd for $C_{16}H_{13}N_2S_2$ $[M+H]^+$: 297.0515. Found: 297.0515.

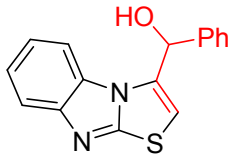
Thiazolo[3,2-*a*]benzimidazol-3-yl-ethanol (3za)



The reaction was performed following slightly modified **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.2 mg, 0.04 mmol), I_2 (50.7 mg, 0.20 mmol), K_2CO_3 (55.9 mg, 0.41 mmol), 3-butyn-1-ol (60.6 μL, d = 0.926 g/mL, 56.1 mg, 0.80 mmol), 2-mercaptobenzimidazole (29.6 mg, 0.20 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 1/3 to pure EA, with 0.5% Et_3N) to afford the title compound as a liquid (21.0 mg, 49%). Mp 128–129 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.5, 3.0 Hz, 2 H), 7.31 (t, *J* = 7.8 Hz, 1 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 6.36 (s, 1 H), 4.15 (t, *J* = 5.8 Hz, 2 H), 4.08-3.92 (brs, 1 H), 3.28 (t, *J* = 5.8 Hz, 2 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.1, 147.9, 131.5, 129.9, 123.4, 120.9, 118.8, 110.9, 106.0, 59.1, 31.8; **HRMS** calcd for $C_{11}H_{11}N_2OS$ $[M+H]^+$: 219.0587. Found: 219.0586.

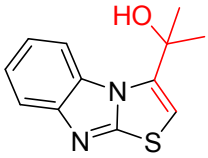
Thiazolo[3,2-*a*]benzimidazol-3-yl-(phenyl)methanol (3Aa)



The reaction was performed following **GP-A** with CuI (4.0 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.5 mg, 0.04 mmol), I_2 (50.7 mg, 0.20 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), 1-phenylprop-2-yn-1-ol (26.2 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.4 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 1/1) to afford the title compound as a liquid (26.6 mg, 48%).

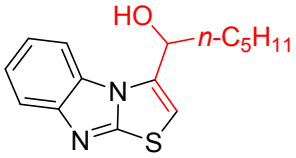
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 7.0 Hz, 2 H), 7.41-7.31 (m, 3 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 7.11 (t, *J* = 7.5 Hz, 1 H), 6.18 (s, 1 H), 6.11 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.2, 147.6, 139.2, 136.0, 129.7, 128.8, 128.7, 126.8, 123.4, 121.0, 118.3, 113.0, 108.9, 69.4; **HRMS** calcd for $C_{16}H_{13}N_2OS$ $[M+H]^+$: 281.0743. Found: 281.0741.

Thiazolo[3,2-*a*]benzimidazol-3-yl-propan-2-ol (3Ba)



The reaction was performed following **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (7.4 mg, 0.04 mmol), I_2 (51.4 mg, 0.20 mmol), K_2CO_3 (55.4 mg, 0.40 mmol), 2-methyl-3-butyn-2-ol (19.4 μL, d = 0.868 g/mL, 16.8 mg 0.20 mmol), 2-mercaptobenzimidazole (38.6 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1) to afford the title compound as a white solid (25.2 mg, 54%). Mp 150–151 °C. **^{1}H NMR (500.13 MHz, $CDCl_3$)** δ 8.32 (d, *J* = 8.5 Hz, 1 H), 7.52 (d, *J* = 7.5 Hz, 1 H), 7.22 (t, *J* = 7.5 Hz, 1 H), 7.14 (t, *J* = 7.8 Hz, 1 H), 6.18 (s, 1 H), 4.46-3.66 (brs, 1 H), 1.67 (s, 6 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.6, 148.0, 140.6, 130.3, 123.3, 120.8, 118.2, 115.9, 104.4, 69.1, 28.7; **HRMS** calcd for $C_{12}H_{13}N_2OS$ $[M+H]^+$: 233.0743. Found: 233.0735.

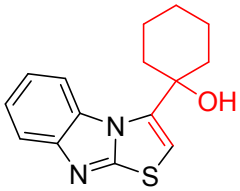
Thiazolo[3,2-*a*]benzimidazol-3-yl-hexan-1-ol (3Ca)



The reaction was performed following **GP-A** with CuI (4.0 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.4 mg, 0.04 mmol), I_2 (51.0 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), 1-octyn-3-ol (25.8 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.4 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1) to afford the title compound as a colourless liquid (30.9 mg, 55%).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1 H), 7.63 (d, *J* = 7.0 Hz, 1 H), 7.30 (t, *J* = 7.3 Hz, 1 H), 7.20 (t, *J* = 7.8 Hz, 1 H), 6.38 (s, 1 H), 5.00 (t, *J* = 6.3 Hz, 1 H), 4.64-3.99 (brs, 1 H), 1.98-1.86 (m, 2 H), 1.67-1.55 (m, 1 H), 1.51-1.40 (m, 1 H), 1.37-1.27 (m, 4 H), 0.89 (t, *J* = 6.8 Hz, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.2, 147.6, 137.1, 129.7, 123.5, 121.1, 118.4, 113.2, 105.5, 67.6, 34.9, 31.5, 25.4, 22.5, 13.9; **HRMS** calcd for $C_{15}H_{19}N_2OS$ $[M+H]^+$: 275.1213. Found: 275.1219.

Thiazolo[3,2-*a*]benzimidazol-3-yl-cyclohexan-1-ol (3Da)

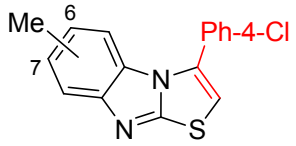


The reaction was performed following slightly modified **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.0 mg, 0.04 mmol), I_2 (50.4 mg, 0.20 mmol), K_2CO_3 (55.6 mg, 0.40 mmol), 1-ethynylcyclohexanol (99.6 mg, 0.80 mmol), 2-mercaptobenzimidazole (29.6 mg, 0.20 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA =

2/1, with 0.5% Et_3N) to afford the title compound as a white solid (33.3 mg, 62%). Mp 240–241 °C.

^{1}H NMR (500.13 MHz, DMSO-*d*$_6$) δ 8.42 (d, *J* = 8.5 Hz, 1 H), 7.65 (d, *J* = 8.0 Hz, 1 H), 7.32 (t, *J* = 7.8 Hz, 1 H), 7.24 (t, *J* = 7.5 Hz, 1 H), 7.02 (s, 1 H), 5.66 (s, 1 H), 2.20-2.11 (m, 2 H), 1.90-1.79 (m, 2 H)，1.78-1.65 (m, 3 H), 1.63-1.54 (m, 2 H), 1.35-1.25 (m, 1 H); **^{13}C NMR (125.76 MHz, DMSO-*d*$_6$)** δ 156.9, 147.9, 141.8, 130.3, 122.9, 120.2, 117.9, 116.0, 104.9, 68.8, 35.3, 25.1, 21.0; **HRMS** calcd for $C_{15}H_{17}N_2OS$ $[M+H]^+$: 273.1062. Found: 273.1086.

3-(4-Chlorophenyl)-6-methyl-thiazolo[3,2-a]benzimidazole (3ab) and 3-(4-Chlorophenyl)-7-methyl-thiazolo[3,2-a]benzimidazole (3ab')[6]



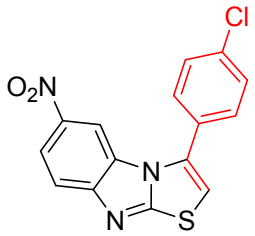
3ab (6-Me) + **3ab'** (7-Me)

The reaction was performed following **GP-A** with CuI (3.9 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.3 mg, 0.04 mmol), I_2 (51.4 mg, 0.20 mmol), K_2CO_3 (56.1 mg, 0.41 mmol), 4-chlorophenylacetylene (27.1 mg, 0.20 mmol), 2-mercapto-5-methylbenzimidazole (43.3 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compounds (inseparable mixture) as a yellow solid (32.9 mg, 56%, 1.1:1).

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 1 H), 7.55-7.44 (m, 9 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 7.02 (d, *J* = 8.0 Hz, 1 H), 6.93 (s, 1 H), 6.84 (d, *J* = 8.0 Hz, 1 H), 6.52 (s, 1 H), 6.51 (s, 1 H), 2.40 (s, 3 H), 2.31 (s, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.9, 156.4, 148.7, 146.5, 136.3, 133.5, 133.0, 133.0, 130.6, 130.04, 130.00, 129.31, 129.27, 127.98, 127.95, 127.86, 127.81, 125.1, 122.1, 119.0, 118.8, 111.5, 111.0, 107.7, 107.5, 21.8, 21.6.

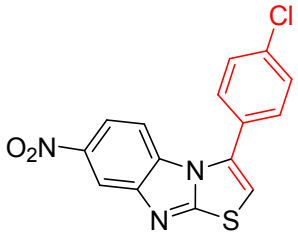
3-(4-Chlorophenyl)-6-nitro-thiazolo[3,2-a]benzimidazole (3ac) and 3-(4-Chlorophenyl)-7-nitro-thiazolo[3,2-a]benzimidazole (3ac')

The reaction was performed following slightly modified **GP-A** with CuI (3.9 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.4 mg, 0.04 mmol), I_2 (52.0 mg, 0.20 mmol), K_2CO_3 (55.7 mg, 0.40 mmol), 4-chlorophenylacetylene (27.9 mg, 0.20 mmol), 2-mercapto-5-nitrobenzimidazole (51.4 mg, 0.26 mmol), and 1 mL of CH_3CN at 100 °C for 46 h. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1 to 1/1, with 0.5% Et_3N) to afford the title compounds **3ac** and **3ac'** (38.8 mg, 58%, 1.1:1).



3ac (6-NO_2)

Yellow solid (18.8 mg, 28%). Mp 272–273 °C.
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.5 Hz, 1 H), 8.23 (s, 1 H), 7.83 (d, *J* = 9.0 Hz, 1 H), 7.66-7.59 (m, 4 H), 6.79 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 161.9, 152.8, 141.3, 137.3, 133.4, 129.9, 129.8, 128.7, 126.6, 119.5, 119.1, 109.5, 108.3; **HRMS** calcd for $C_{15}H_9ClN_3O_2S$ $[M+H]^+$: 330.0099. Found: 330.0105.

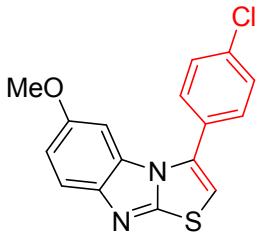


3ac' (7-NO_2)

Yellow solid (20.0 mg, 30%), Mp 234-237 °C.
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.0 Hz, 1 H), 7.96 (dd, *J* = 9.0, 1.5 Hz, 1 H), 7.58-7.49 (m, 4 H), 7.21 (d, *J* = 9.5 Hz, 1 H), 6.73 (s, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 160.2, 148.0, 144.3, 137.0, 133.4, 132.8, 130.1, 129.7, 126.9, 116.0, 115.7, 111.3, 109.9; **HRMS** calcd for $C_{15}H_9ClN_3O_2S$ $[M+H]^+$: 330.0099. Found: 330.0107.

3-(4-Chlorophenyl)-6-methoxy-thiazolo [3,2-a] benzimidazole (3ad) and 3-(4-Chlorophenyl)-7-methoxy-thiazolo[3,2-a]benzimidazole (3ad')

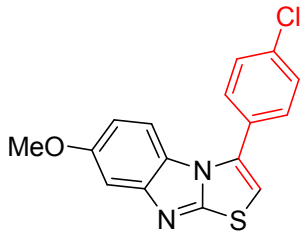
The reaction was performed following slightly modified **GP-A** with CuI (7.9 mg, 0.04 mmol), 1,10-phen (**L-1**) (14.4 mg, 0.08 mmol), I_2 (52.0 mg, 0.20 mmol), K_2CO_3 (55.8 mg, 0.40 mmol), 4-chlorophenylacetylene (27.6 mg, 0.20 mmol), 2-mercapto-5-methoxybenzimidazole (46.5 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C for 26 h. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1, with 0.5% Et_3N) to afford the title compounds **3ad** and **3ad'** (41.0 mg, 64%, 1.3:1).



3ad (6-OMe)

Yellow solid (18.1 mg, 28%). Mp 212–213 °C.
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.5 Hz, 1 H), 7.59 (d, *J* = 8.5 Hz, 2 H),

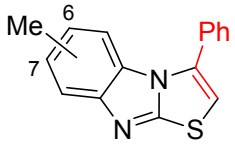
7.55 (d, J = 8.5 Hz, 2 H), 6.98 (d, J = 8.5 Hz, 1 H), 6.70 (s, 1 H), 6.59 (s, 1 H), 3.71 (s, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 154.6, 136.4, 132.7, 130.1, 130.0, 129.4, 129.2, 127.8, 119.6, 112.0, 107.9, 96.5, 55.9; **HRMS** calcd for $C_{16}H_{12}ClN_2OS$ $[M+H]^+$: 315.0353. Found: 315.0350.



3ad' (7-OMe)

Yellow solid (22.9 mg, 36%). Mp 213–214 °C.
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2 H), 7.54 (d, J = 8.0 Hz, 2 H), 7.40-7.27 (m, 1 H), 7.25-7.14 (m, 1 H), 6.71 (d, J = 9.0 Hz, 1 H), 6.57 (s, 1 H), 3.71 (s, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.7, 136.3, 133.1, 130.1, 130.0, 129.3, 129.2, 127.9, 112.1, 110.5, 107.2, 101.7, 55.7; **HRMS** calcd for $C_{16}H_{12}ClN_2OS$ $[M+H]^+$: 315.0353. Found: 315.0356.

3-(4-Chlorophenyl)-6-methyl-thiazolo[3,2-a]benzimidazole (3jb) and 3-(4-Chlorophenyl)-7-methyl-thiazolo[3,2-a]benzimidazole (3jb')[6]



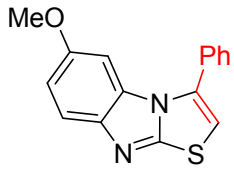
3jb (6-Me) + **3jb'** (7-Me)

The reaction was performed following **GP-A** with CuI (3.7 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.4 mg, 0.04 mmol), I_2 (51.2 mg, 0.20 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), phenylacetylene (21.9 μL, d = 0.93 g/mL, 20.4 mg, 0.20 mmol), 2-mercapto-5-methylbenzimidazole (43.2 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 5/1 to 3/1) to afford the title compounds (inseparable mixture) as a white solid (28.8 mg, 54%, 1.2:1).
^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.69-7.61 (m, 5 H), 7.60-7.52 (m, 7 H), 7.14 (d, J = 8.5 Hz, 1 H), 7.10 (d, J = 8.5 Hz, 1 H), 7.00 (s, 1 H), 6.88 (d, J = 8.0 Hz, 1 H), 6.554 (s, 1 H), 6.549 (s, 1 H), 2.47 (s, 3 H), 2.36 (s, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ = 157.1, 156.6, 149.1, 146.9, 134.2, 134.1, 133.1, 130.2, 130.04, 130.00, 129.54, 129.52, 128.91, 128.88, 128.8, 128.7, 128.2, 124.8, 121.8, 119.0, 118.7, 111.6, 111.1, 106.9, 106.7, 21.7, 21.6.

3-Phenyl-6-methoxy-thiazolo[3,2-a]benzimidazole (3jd) and 3-phenyl-7-methoxy-thiazolo[3,2-a]benzimidazole (3jd')

The reaction was performed following **GP-A** with CuI (3.8 mg, 0.02 mmol), 1,10-phen (**L-1**) (7.4 mg, 0.04 mmol), I_2 (51.3 mg, 0.20 mmol), K_2CO_3 (55.2 mg, 0.40 mmol), phenylacetylene (21.9 μL, d = 0.93 g/mL, 20.4 mg, 0.20 mmol), 2-mercapto-

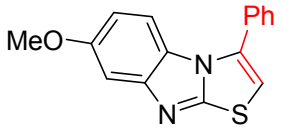
5-methoxybenzimidazole (47.0 mg, 0.26 mmol), and 1 mL of CH_3CN at 80 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 10/1 to 3/1) to afford the title compounds **3jd** and **3jd'** (29.6 mg, 53%, 1.5:1).



3jd (6-MeO)

White solid (11.8 mg, 21%). Mp 109–110 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.70-7.62 (m, 3 H), 7.60-7.54 (m, 3 H), 6.97 (dd, *J* = 8.8, 2.8 Hz, 1 H), 6.69 (d, *J* = 2.0 Hz, 1 H), 6.58 (s, 1 H), 3.67 (s, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 155.9, 154.5, 143.1, 133.9, 130.3, 130.2, 129.4, 128.94, 128.90, 119.5, 112.1, 107.2, 96.4, 55.8; **HRMS** calcd for $C_{16}H_{13}N_2OS$ $[M+H]^+$: 281.0743. Found: 281.0740.

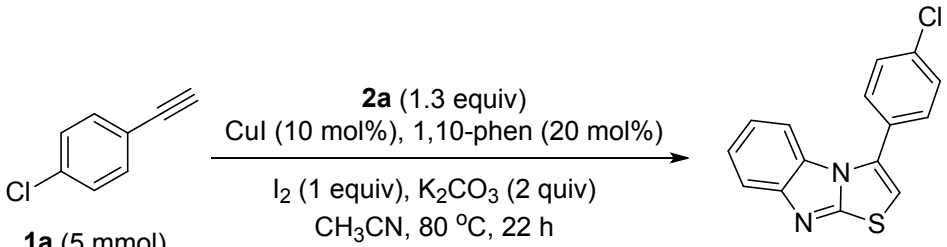


3jd' (7-MeO)

White solid (17.8 mg, 32%). Mp 137–139 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.60-7.54 (m, 2 H), 7.53-7.46 (m, 3 H), 7.22-7.16 (m, 1 H), 7.05 (d, *J* = 9.0 Hz, 1 H), 6.63 (d, *J* = 9.0 Hz, 1 H), 6.51 (s, 1 H), 3.79 (s, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.3, 156.7, 149.8, 134.2, 130.1, 129.5, 129.0, 128.7, 124.8, 112.0, 110.1, 106.5, 101.5, 55.7; **HRMS** calcd for $C_{16}H_{13}N_2OS$ $[M+H]^+$: 281.0743. Found: 281.0741.

Gram-scale synthesis of 3aa



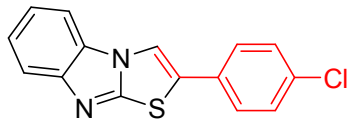
1a (5 mmol)

3aa, 70% (1.0 g)

To a Schlenk tube (50 mL) were added I_2 (1.0 mmol), K_2CO_3 (10.0 mmol), 2-mercaptobenzimidazole **2a** (6.5 mmol), CuI (0.5 mmol), 1,10-phen (**L-1**) (1.0 mmol), 4-chlorophenylacetylene **1a** (mg, 5 mmol), and 10 mL of CH_3CN sequentially under air and then the resulting mixture was stirred at room temperature for 5 min. The tube was then sealed and the reaction mixture was stirred at 80 °C for 22 h. After cooling to room temperature, the mixture was filtered through Celite and the filtrate was concentrated. The crude mixture was purified by flash column chromatography on silica gel (PE/EA = 4/1, with 0.5% Et_3N) to afford **3aa** as a white solid (1.0 g, 70%).

Syntheses and characterization of 2-substituted thiazolo[3, 2-a]benzimidazoles (4)

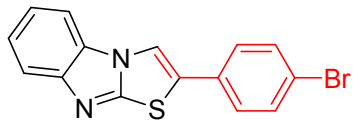
2-(4-Chlorophenyl)thiazolo[3, 2-a]benzimidazole (4aa)



The reaction was performed following **GP-C** with CuI (9.3 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (16.0 mg, 0.06 mmol), I_2 (51.4 mg, 0.20 mmol), K_2CO_3 (55.6 mg, 0.40 mmol), 4-chlorophenylacetylene (27.5 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.2 mg, 0.26 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (40.6 mg, 71%), along with **3aa** (8.2 mg, 14%). Mp 226–227 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.92 (s, 1 H), 7.80 (d, *J* = 8.5 Hz, 1 H), 7.68 (d, *J* = 8.0 Hz, 1 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 7.43 (d, *J* = 9.0 Hz, 2 H), 7.39 (t, *J* = 7.8 Hz, 1 H), 7.30 (t, *J* = 7.8 Hz, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 155.4, 147.0, 134.8, 129.6, 129.5, 128.6, 127.0, 123.9, 121.5, 119.2, 111.8, 110.3; **HRMS** calcd for $C_{15}H_{10}ClN_2S$ $[M+H]^+$: 285.0248. Found: 285.0258.

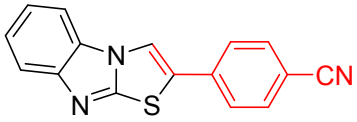
2-(4-Bromophenyl)thiazolo[3, 2-a]benzimidazole (4ba)



The reaction was performed following **GP-C** with CuI (9.7 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (16.2 mg, 0.06 mmol), I_2 (51.0 mg, 0.20 mmol), K_2CO_3 (54.8 mg, 0.40 mmol), 4-bromophenylacetylene (35.9 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.2 mg, 0.26 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound as a white solid (38.5 mg, 59%), along with **3ba** (13.3 mg, 20%). Mp 223–224 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.91 (s, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 7.0 Hz, 2 H), 7.42 (d, *J* = 7.5 Hz, 2 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.29 (t, *J* = 7.3 Hz, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 155.4, 147.5, 132.4, 130.2, 129.6, 128.3, 127.2, 123.8, 122.8, 121.4, 119.4, 112.8, 110.2; **HRMS** calcd for $C_{15}H_{10}BrN_2S$ $[M+H]^+$: 328.9743. Found: 328.9740.

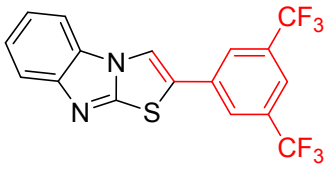
2-(4-Cyanophenyl)thiazolo[3, 2-a]benzimidazole (4da)



The reaction was performed following **GP-C** with CuI (9.8 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (16.0 mg, 0.06 mmol), I_2 (51.9 mg, 0.20 mmol), K_2CO_3 (55.4 mg, 0.40 mmol), 4-cyanophenylacetylene (25.8 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.3 mg, 0.26 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 2/1, with 0.5% Et_3N) to afford the title compound as a yellow solid (39.5 mg, 71%), along with **3da** (3.5 mg, 6%). Mp 234–236 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.04 (s, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.72 (d, *J* = 8.5 Hz, 1 H), 7.67 (d, *J* = 7.5 Hz, 2 H), 7.64 (d, *J* = 9.0 Hz, 2 H), 7.39 (t, *J* = 7.3 Hz, 1 H), 7.30 (t, *J* = 7.3 Hz, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 155.3, 147.7, 135.7, 133.0, 129.5, 127.2, 126.0, 124.2, 121.7, 119.5, 118.2, 114.6, 112.0, 110.3; **HRMS** calcd for $C_{16}H_{10}N_3S$ $[M+H]^+$: 276.0590. Found: 276.0588.

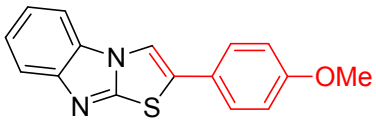
2-(3,5-bis(trifluoromethyl)phenyl)thiazolo[3, 2-a]benzimidazole (4ka)



The reaction was performed following **GP-C** with CuI (9.6 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (16.2 mg, 0.06 mmol), I_2 (50.3 mg, 0.20 mmol), K_2CO_3 (55.5 mg, 0.40 mmol), 3,5-bis(trifluoromethyl)phenylacetylene (47.3 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.0 mg, 0.26 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound as a yellow solid (57.1 mg, 74%), along with **3ka** (8.7 mg, 11%). Mp 223–226 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.22 (s, 1 H), 8.02 (s, 2 H), 7.93 (s, 1 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.80 (d, *J* = 8.0 Hz, 1 H), 7.52 (t, *J* = 7.8 Hz, 2 H), 7.44 (t, *J* = 7.5 Hz, 2 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 155.0, 147.9, 133.6, 132.9 (q, *J* = 33.8 Hz), 129.6, 122.9 (q, *J* = 272.6 Hz), 125.9, 125.6, 125.5, 124.2, 122.1 (sep, *J* = 3.8 Hz), 121.8, 119.6, 114.8, 110.3; **HRMS** calcd for $C_{17}H_9F_6N_2S$ $[M+H]^+$: 387.0385. Found: 287.0394.

2-(4-Methoxyphenyl)thiazolo[3, 2-a]benzimidazole (4ga)

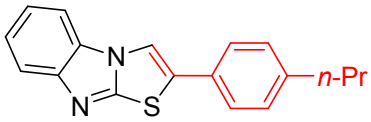


The reaction was performed following **GP-C** with CuI (9.3 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (16.2 mg, 0.06 mmol), I_2 (51.5 mg, 0.20 mmol), K_2CO_3 (56.2 mg, 0.41 mmol), 4-methoxyphenylacetylene (27.0 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.0 mg, 0.26 mmol), and 1 mL of DMSO at 40 °C. The

crude product was purified by flash column chromatography on silica gel (PE/EA = 3/1) to afford the title compound as a white solid (13.6 mg, 71%), along with **3ga** (29.5 mg, 52%). Mp 152–155 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1 H), 7.69 (s, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.41 (d, *J* = 9.0 Hz, 2 H), 7.28 (t, *J* = 7.8 Hz, 1 H), 7.19 (t, *J* = 7.5 Hz, 1 H), 8.89 (d, *J* = 9.0 Hz, 1 H), 3.78 (s, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 160.2, 155.7, 147.5, 129.7, 129.6, 127.3, 123.8, 123.4, 121.1, 119.2, 114.7, 111.2, 110.1, 55.4; **HRMS** calcd for $C_{16}H_{13}N_2OS$ $[M+H]^+$: 281.0743. Found: 281.0741.

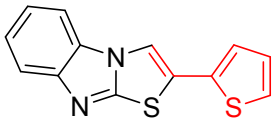
2-(4-Propylphenyl)thiazolo[3, 2-a]benzimidazole (4ha)



The reaction was performed following **GP-C** with CuI (9.5 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (15.8 mg, 0.06 mmol), I_2 (51.9 mg, 0.20 mmol), K_2CO_3 (54.8 mg, 0.40 mmol), 4-propylphenylacetylene (28.4 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.5 mg, 0.26 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound as a white solid (25.3 mg, 44%), along with **3ha** (22.1 mg, 38%). Mp 134–136 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.76 (s, 1 H), 7.71 (d, *J* = 8.5 Hz, 1 H), 7.57 (d, *J* = 7.5 Hz, 1 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.28 (t, *J* = 7.5 Hz, 1 H), 7.22-7.13 (m, 3 H), 2.54 (t, *J* = 7.5 Hz, 2 H), 1.64-1.54 (m, 2 H), 0.88 (t, *J* = 7.3 Hz, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 155.6, 147.3, 143.8, 129.9, 129.6, 129.3, 128.5, 125.8, 123.5, 121.2, 119.2, 111.8, 110.2, 37.7, 24.3, 13.7; **HRMS** calcd for $C_{18}H_{17}N_2S$ $[M+H]^+$: 293.1107. Found: 293.1107.

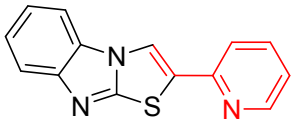
2-Thiophen-2-ylthiazolo[3,2-a]benzimidazole (4la)



The reaction was performed following **GP-C** with CuI (9.5 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (15.9 mg, 0.06 mmol), I_2 (52.0 mg, 0.20 mmol), K_2CO_3 (56.0 mg, 0.41 mmol), 2-ethynylthiophene (22.0 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.2 mg, 0.26 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound as a yellow solid (25.2 mg, 48%), along with **3la** (11.7 mg, 22%). Mp 147–150 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.81-7.73 (m, 2 H), 7.63 (d, *J* = 8.5 Hz, 1 H), 7.36 (d, *J* = 7.3 Hz, 1 H), 7.32 (d, *J* = 5.0 Hz, 1 H), 7.27 (d, *J* = 7.5 Hz, 1 H), 7.20 (d, *J* = 3.0 Hz, 1 H), 7.07 (dd, *J* = 5.0, 3.5 Hz, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 155.2, 147.5, 133.1, 129.6, 128.0, 125.84, 125.80, 123.7, 123.0, 121.4, 119.3, 112.5, 110.2; **HRMS** calcd for $C_{13}H_9N_2S_2$ $[M+H]^+$: 257.0202. Found: 257.0210.

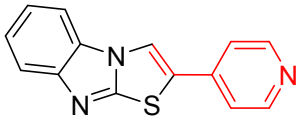
2-Pyridin-2-ylthiazolo[3,2-a]benzimidazole (4na)



The reaction was performed following **GP-C** with CuI (9.8 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (16.0 mg, 0.06 mmol), I_2 (51.9 mg, 0.20 mmol), K_2CO_3 (55.8 mg, 0.40 mmol), 2-ethynylpyridine **1n** (20.4 mg, 0.20 mmol), 2-mercaptobenzimidazole **2a** (39.4 mg, 0.26 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 1/1, with 0.5% Et_3N) to afford the title compound as a yellow solid (39.8 mg, 80%), along with **3na** (2.6 mg, 5%). Mp 213–214 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.50 (d, *J* = 5.0 Hz, 1 H), 8.13 (s, 1 H), 7.70 (d, *J* = 8.5 Hz, 1 H), 7.64 (td, *J* = 7.5, 1.0 Hz, 1 H), 7.57 (d, *J* = 8.0 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.29 (t, *J* = 7.5 Hz, 1 H), 7.19 (t, *J* = 7.8 Hz, 1 H), 7.13 (dd, *J* = 6.8, 5.3 Hz, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.5, 149.9, 149.7, 147.8, 136.7, 130.7, 129.6, 123.8, 122.8, 121.3, 119.3, 118.7, 114.5, 110.2; **HRMS** calcd for $C_{14}H_{10}N_3S$ $[M+H]^+$: 252.0950. Found: 252.0953.

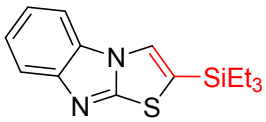
2-Pyridin-4-ylthiazolo[3,2-a]benzimidazole (4oa)



The reaction was performed following **GP-C** with CuI (9.6 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (16.2 mg, 0.06 mmol), I_2 (50.7 mg, 0.20 mmol), K_2CO_3 (54.6 mg, 0.40 mmol), 4-ethynylpyridine (20.5 mg, 0.20 mmol), 2-mercaptobenzimidazole (39.1 mg, 0.26 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 1/2, with 0.5% Et_3N) to afford the title compound as a yellow solid (41.9 mg, 84%), along with **3oa** (3.8 mg, impure, <8%). Mp 188–190 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 8.73-8.57 (m, 2 H), 8.12 (s, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J* = 7.5 Hz, 1 H), 7.47-7.35 (m, 3 H), 7.29 (t, *J* = 7.8 Hz, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 155.3, 150.6, 147.9, 138.7, 129.5, 126.3, 124.2, 121.6, 119.6, 115.0, 110.3; **HRMS** calcd for $C_{14}H_{10}N_3S$ $[M+H]^+$: 252.0590. Found: 252.0599; **HRMS** calcd for $C_{14}H_{10}N_3S$ $[M+H]^+$: 252.0950. Found: 252.0951.

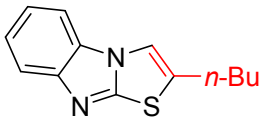
2-(Triethylsilyl)thiazolo[3,2-a]benzimidazole (4qa)



The reaction was performed following slightly modified **GP-C** with CuI (9.5 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (15.6 mg, 0.06 mmol), I_2 (51.1 mg, 0.20 mmol), K_2CO_3 (54.9 mg, 0.40 mmol), 2-mercaptobenzimidazole (38.4 mg, 0.26 mmol), (triethylsilyl)acetylene (27.9 mg, 0.20 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 5/1) to afford the title compound as a colourless liquid (40.9 mg, 71%) (Regioisomer **3qa** was not observed.)

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1 H), 7.66 (d, *J* = 7.5 Hz, 1 H), 7.60 (s, 1 H), 7.35 (d, *J* = 7.5 Hz, 1 H), 7.24 (t, *J* = 7.8 Hz, 1 H), 1.04 (t, *J* = 8.0 Hz, 1 H), 0.86 (q, *J* = 7.8 Hz, 1 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 160.1, 148.9, 129.1, 123.6, 121.8, 120.7, 119.1, 110.3, 7.1, 3.7; **HRMS** calcd for $C_{15}H_{21}N_2SSi$ $[M+H]^+$: 289.1190. Found: 289.1195.

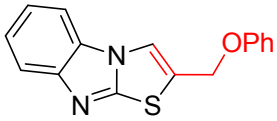
2-Butylthiazolo[3,2-a]benzimidazole (4ua)[5]



The reaction was performed following **GP-C** with CuI (9.6 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (16.1 mg, 0.06 mmol), I_2 (52.0 mg, 0.20 mmol), K_2CO_3 (55.7 mg, 0.40 mmol), 2-mercaptobenzimidazole (39.0 mg, 0.26 mmol), hex-1-yne (22.5 μL, d = 0.715 g/mL, 16.1 mg, 0.20 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound as a white solid (19.1 mg, 42%), along with **3ua** (5.1 mg, 11%). Mp 93–94 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1 H), 7.58 (d, *J* = 8.0 Hz, 1 H), 7.39 (s, 1 H), 7.33 (t, *J* = 7.8 Hz, 1 H), 7.23 (t, *J* = 7.8 Hz, 1 H), 2.78 (t, *J* = 7.3 Hz, 2 H), 1.75-1.65 (m, 2 H), 1.49-1.39 (m, 2 H), 0.97 (t, *J* = 7.5 Hz, 3 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.3, 147.2, 130.8, 129.5, 123.1, 120.8, 119.0, 113.0, 110.0, 32.2, 28.5, 22.0, 13.6.

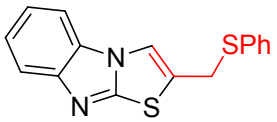
2-Phenoxymethylthiazolo[3,2-a]benzimidazole (4xa)



The reaction was performed following **GP-C** with CuI (9.5 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (16.4 mg, 0.06 mmol), I_2 (51.5 mg, 0.20 mmol), K_2CO_3 (54.6 mg, 0.40 mmol), 2-mercaptobenzimidazole (38.5 mg, 0.26 mmol), phenyl propargyl ether (27.1 mg, 0.20 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 1/1) to afford the title compound as a white solid (32.9 mg, 57%), along with **3xa** (3.0 mg, 5%). Mp 184–185 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1 H), 7.64 (s, 1 H), 7.54 (d, *J* = 8.0 Hz, 1 H), 7.32-7.22 (m, 3 H), 7.19 (t, *J* = 7.5 Hz, 1 H), 6.99-6.89 (m, 3 H), 5.10 (s, 2 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 157.7, 156.5, 129.7, 125.0, 123.7, 122.1, 121.2, 119.3, 116.0, 115.1, 110.1, 63.9; **HRMS** calcd for $C_{16}H_{13}N_2OS$ $[M+H]^+$: 281.0743. Found: 281.0744.

2-Phenylthiomethylthiazolo[3,2-a]benzimidazole (4ya)

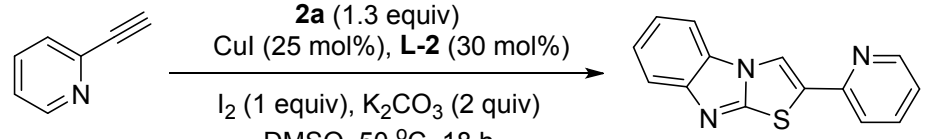


The reaction was performed following **GP-C** with CuI (9.5 mg, 0.05 mmol), 2,9-diisopropyl-1,10-phen (**L-2**) (15.5 mg, 0.06 mmol), I_2 (51.3 mg, 0.20 mmol), K_2CO_3

(56.1 mg, 0.41 mmol), 2-mercaptobenzimidazole (38.9 mg, 0.26 mmol), phenyl propargyl sulfide (29.2 mg, 0.20 mmol), and 1 mL of DMSO at 40 °C. The crude product was purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the title compound as a white solid (39.5 mg, 68%), along with **3ya** (4.4 mg, 7%). Mp 148–149 °C.

^{1}H NMR (500.13 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 8.5 Hz, 1 H), 7.36-7.28 (m, 3 H), 7.25 (t, *J* = 7.5 Hz, 1 H), 7.23-7.16 (m, 3 H), 7.14 (t, *J* = 7.8 Hz, 1 H), 4.10 (s, 2 H); **^{13}C NMR (125.76 MHz, $CDCl_3$)** δ 156.1, 147.1, 133.8, 131.5, 129.3, 129.2, 127.8, 127.3, 123.5, 121.1, 119.1, 115.0, 110.1, 33.4; **HRMS** calcd for $C_{16}H_{13}N_2S_2$ $[M+H]^+$: 297.0515. Found: 297.0520.

Gram-scale synthesis of 4na



1n (5 mmol)

4na, 78% (0.98 g)
(contaminated with trace of **3na**)

To a 100 mL round-bottomed flask were added 2-mercaptobenzimidazole **2a** (978.0 mg， 6.51 mmol), I_2 (1.2672 g, 4.99 mmol), K_2CO_3 (1.3811 g, 10.06 mmol), CuI (238.7 mg, 1.25 mmol), 2,9-diisopropyl-1,10-phenanthroline (**L-2**) (398.0 mg, 1.51 mmol), 2-ethynylpyridine **1n** (515.6 mg, 5.00 mmol), and 25 mL of DMSO sequentially under air and then the resulting mixture was stirred at room temperature for 5 minutes. The flask was then sealed with a rubber stopper and the reaction mixture was stirred at 50 °C for 18 h. After cooling to room temperature, the reaction mixture was diluted with EA (120 mL), washed with water (50 mL) and brine (2 x 50 mL), dried over anhydrous Na_2SO_4. Filtration, concentration, and purification by flash column chromatography on silica gel (PE/EA = 2/1, with 0.5% Et_3N) afforded the desired product as a yellow solid (0.975 g, 78%, contaminated with trace of **3na**).

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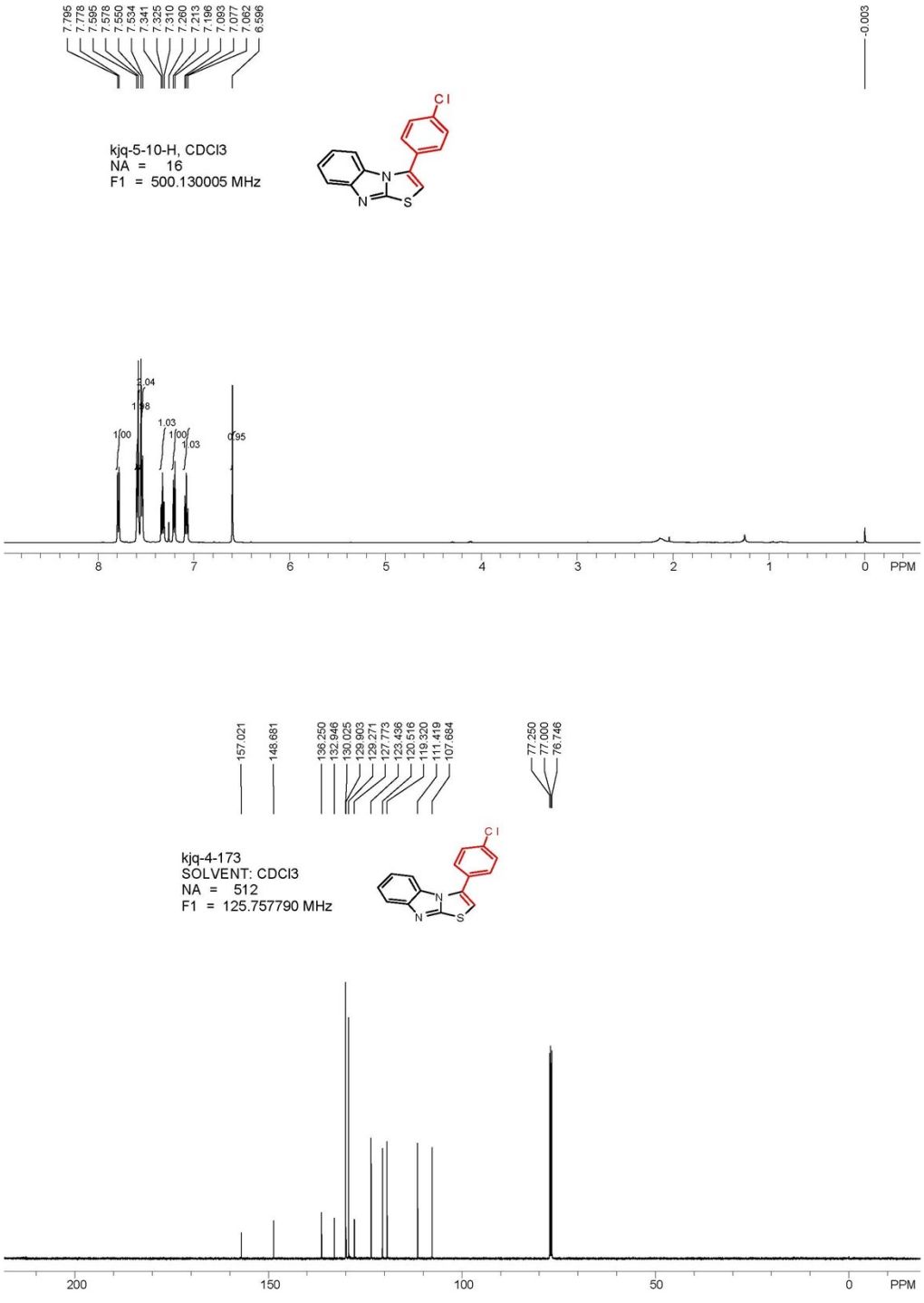
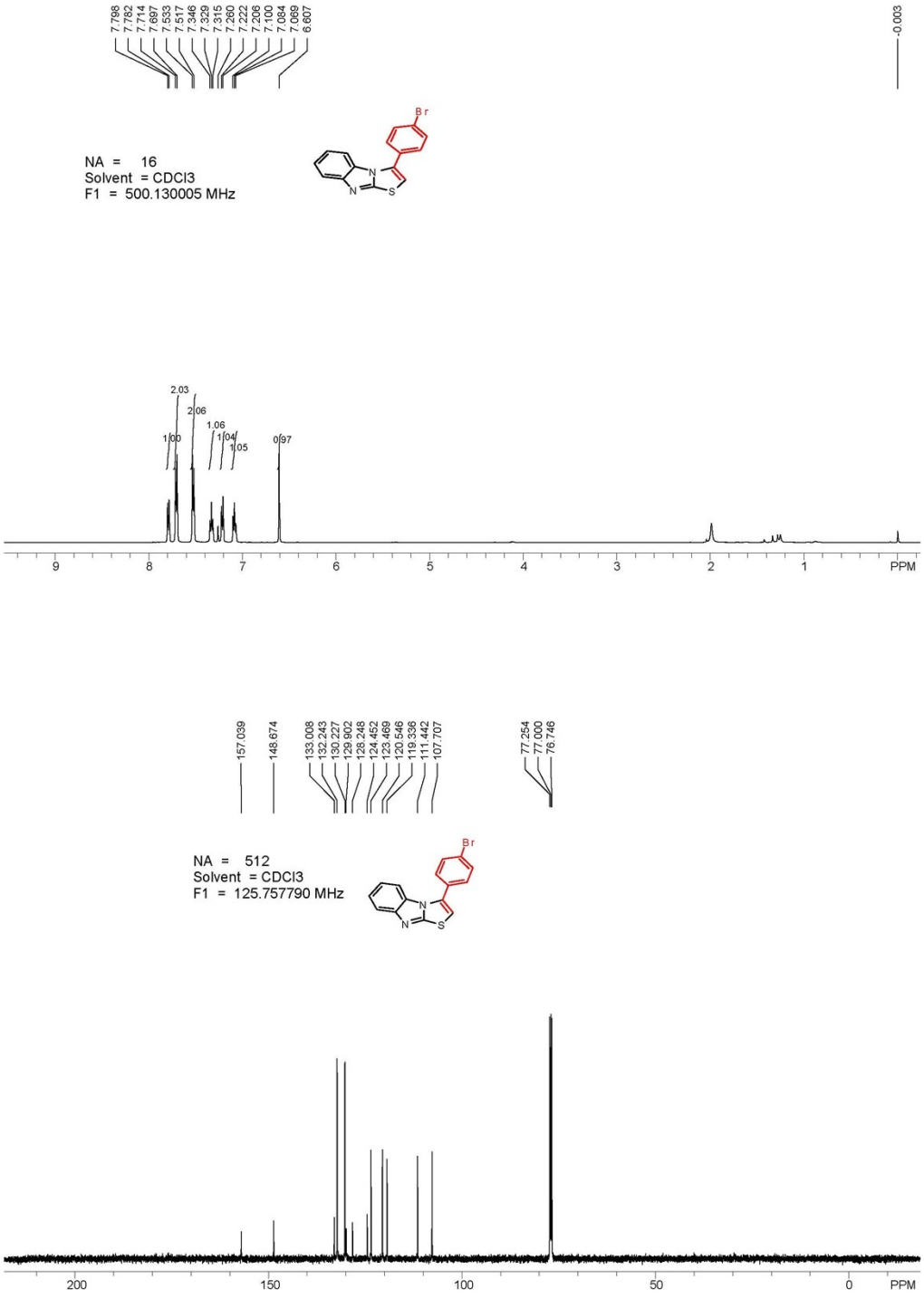
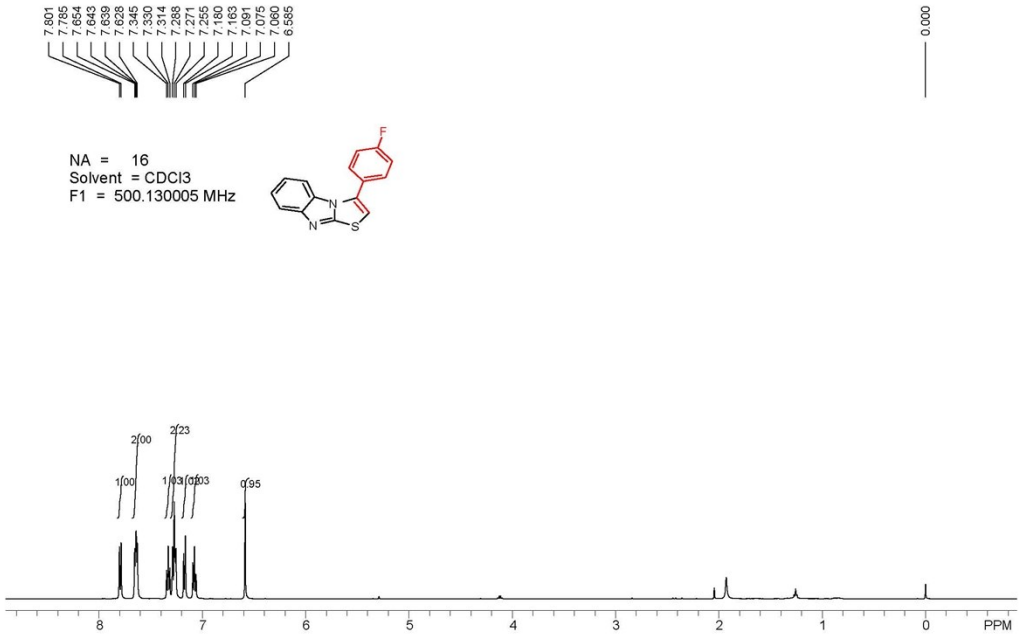
3-(4-Chlorophenyl)thiazolo[3,2-a]benzimidazole (3aa)

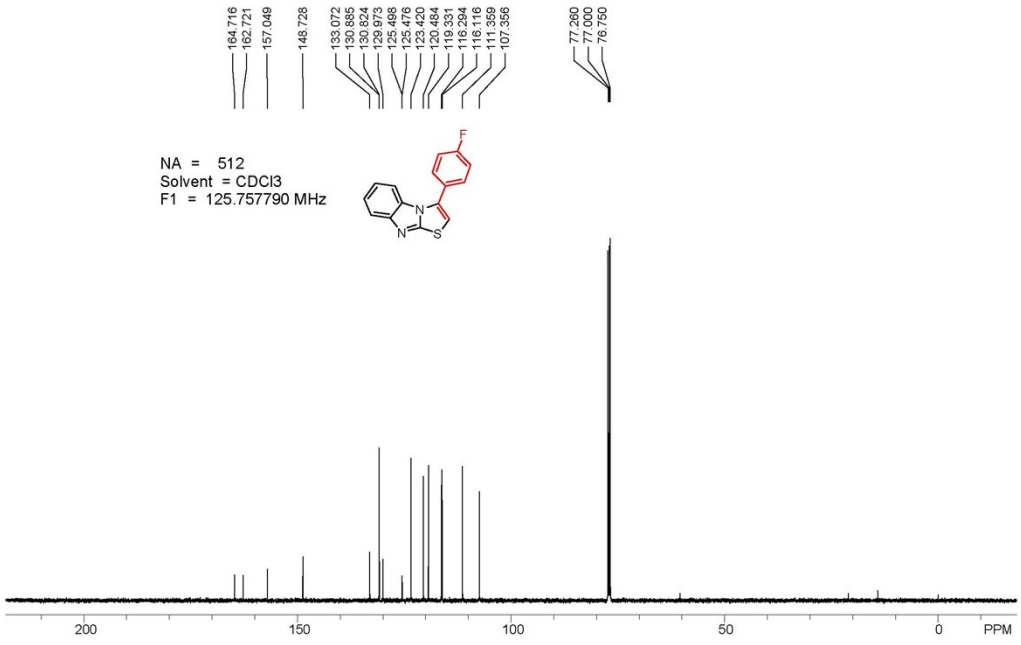


3-(4-Bromophenyl)thiazolo[3,2-a]benzimidazole (3ba)



3-(4-Fluorophenyl)thiazolo[3,2-a]benzimidazole (3ca)





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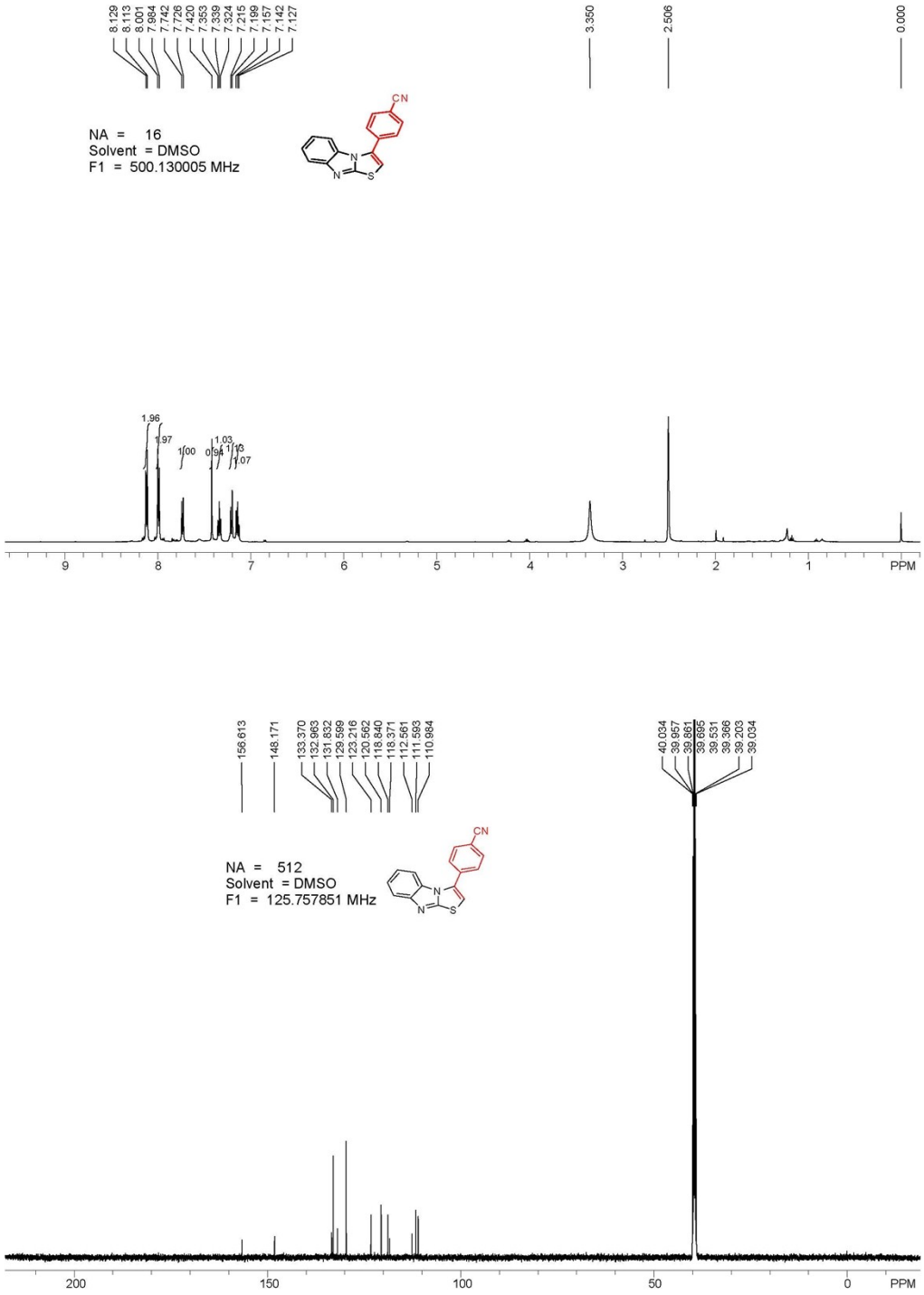

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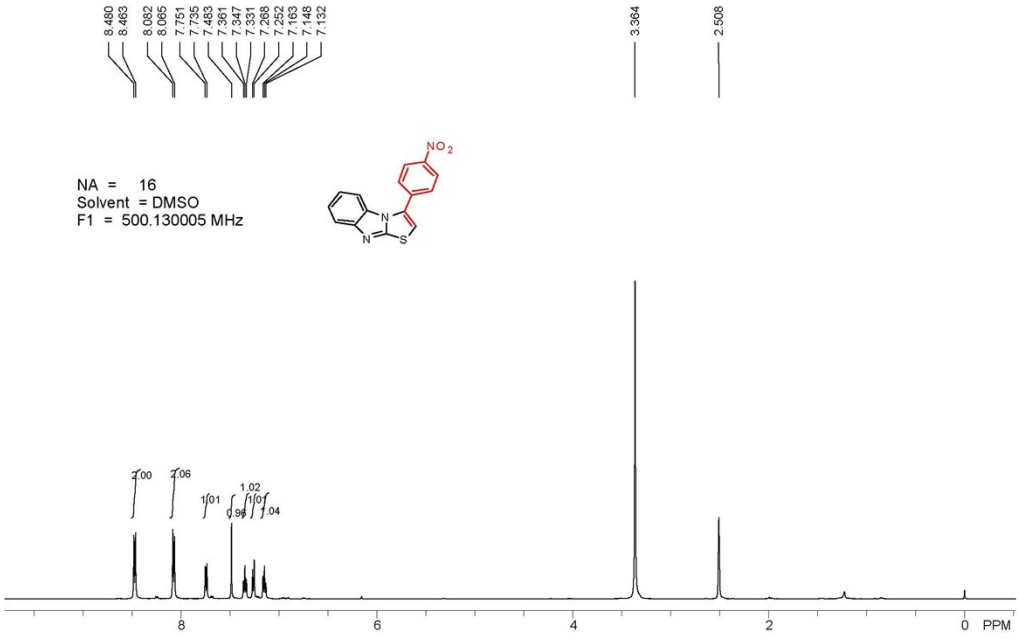

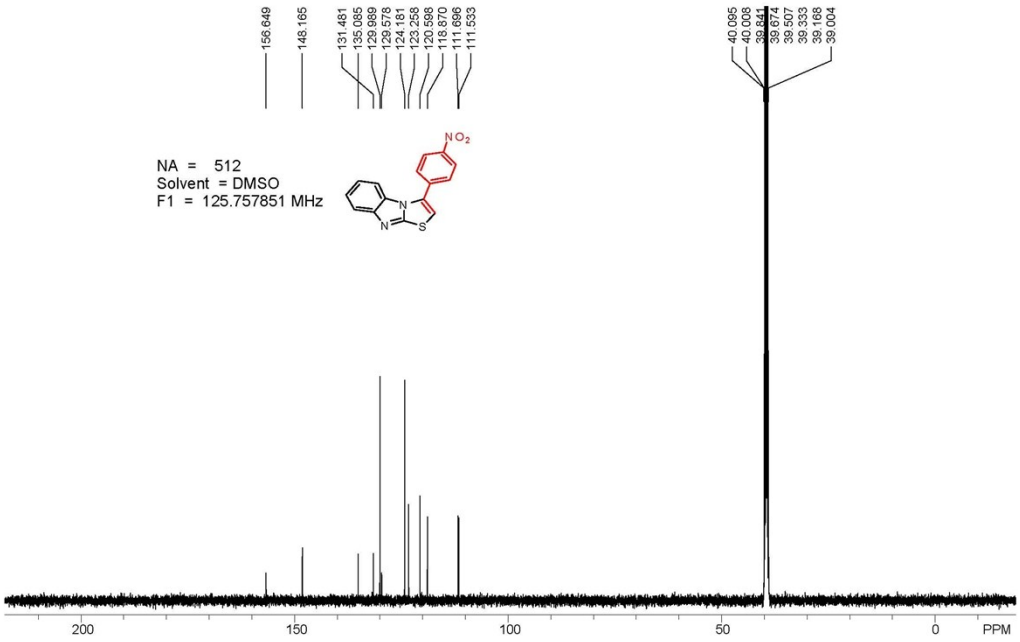

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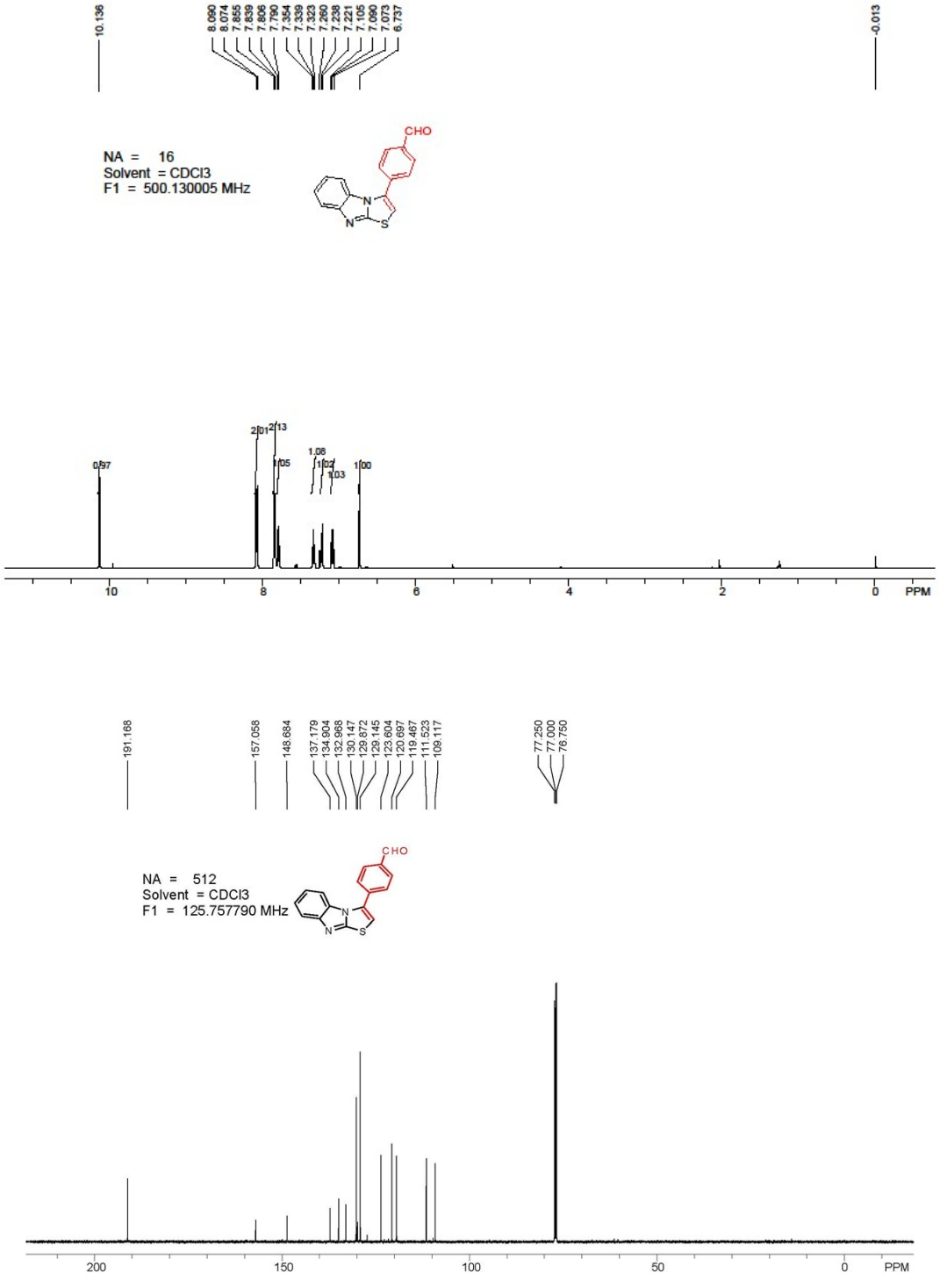

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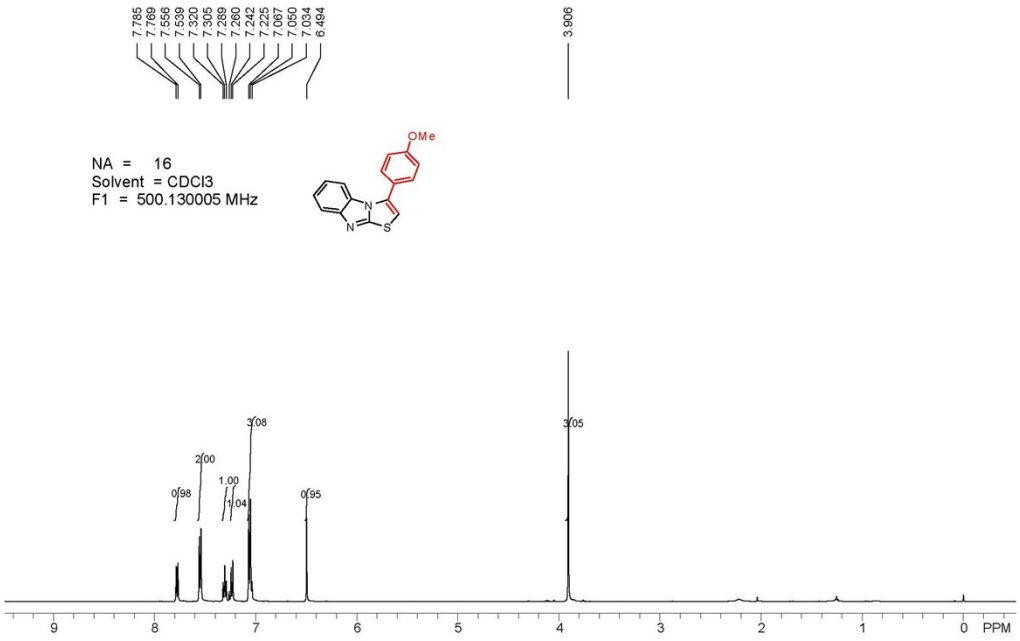

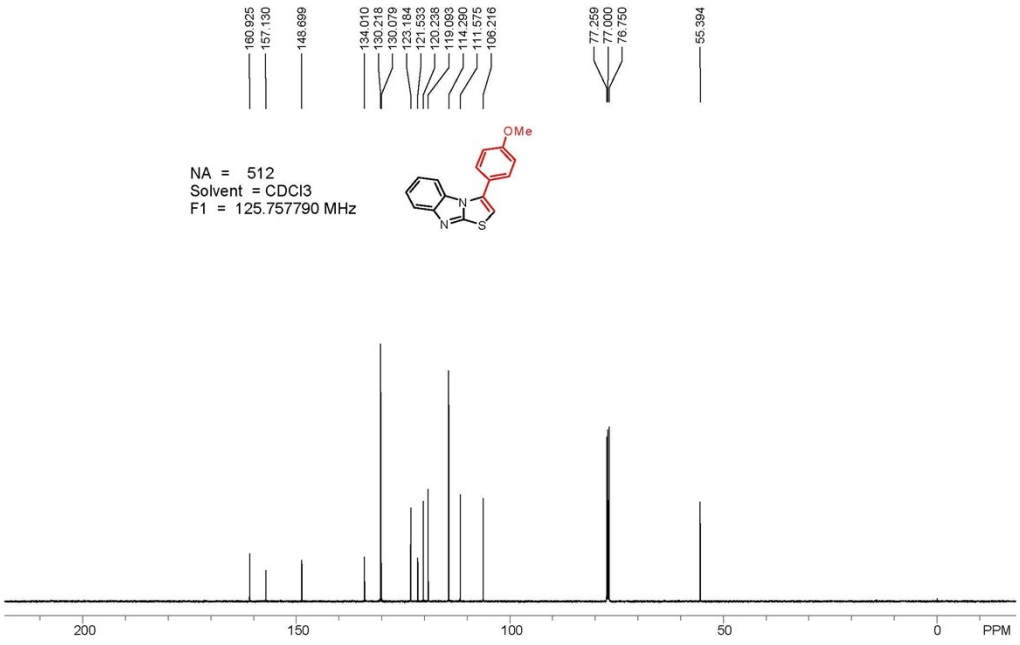

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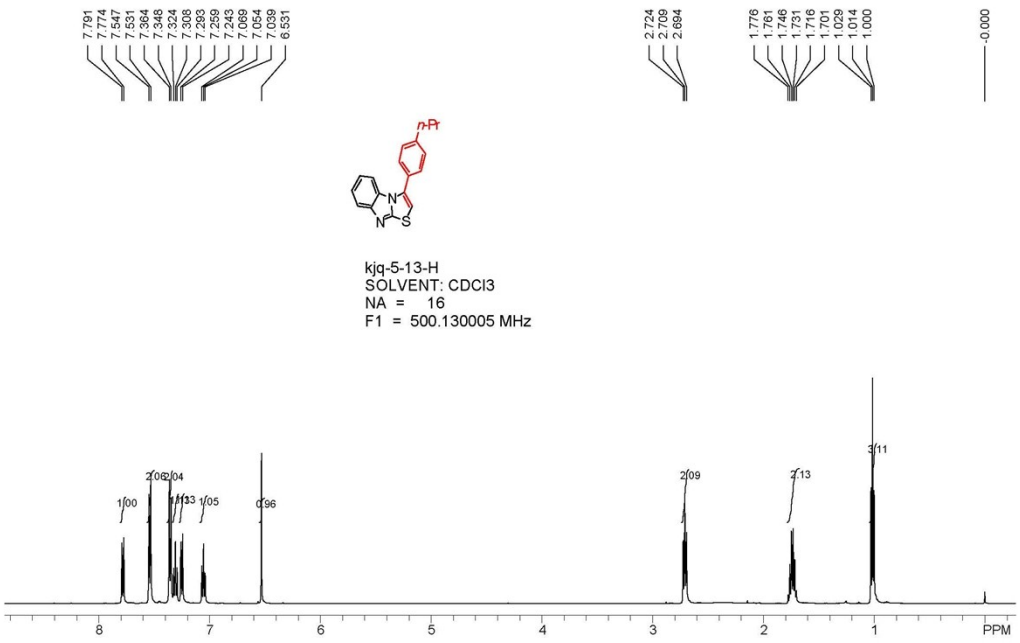

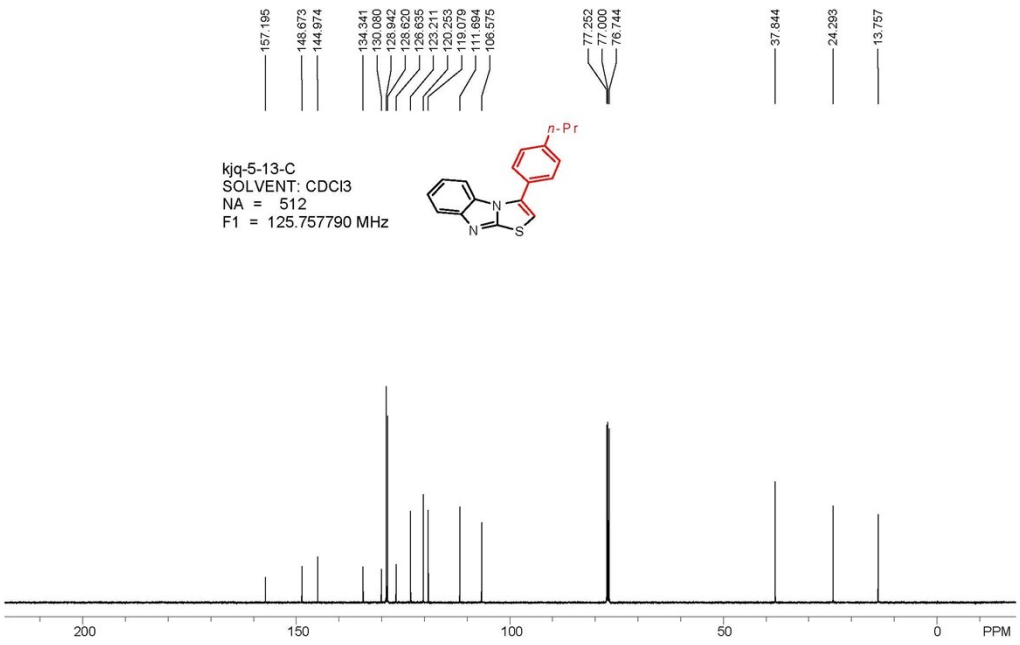

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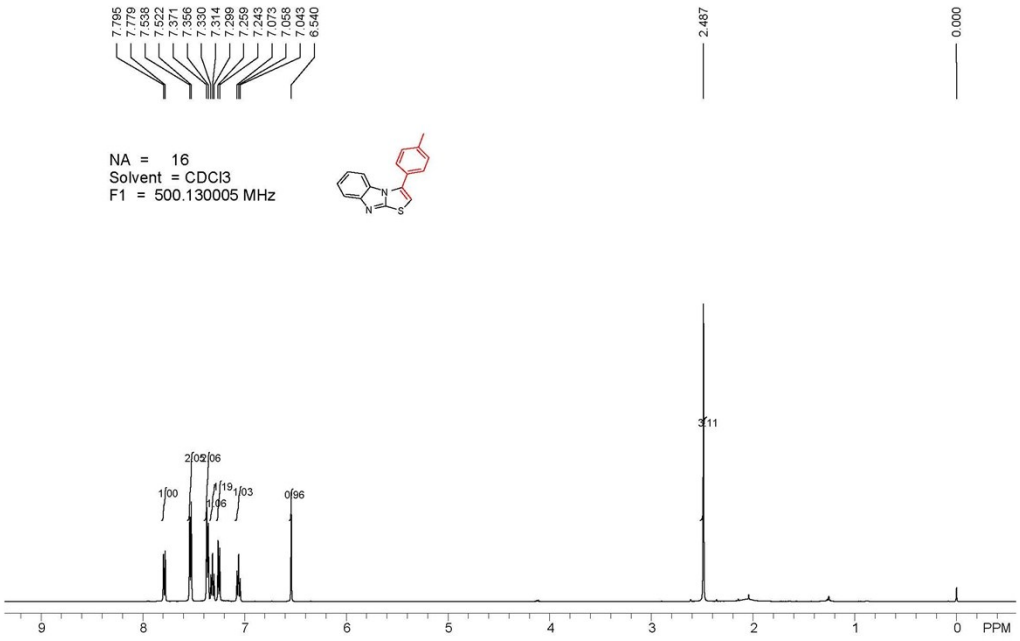

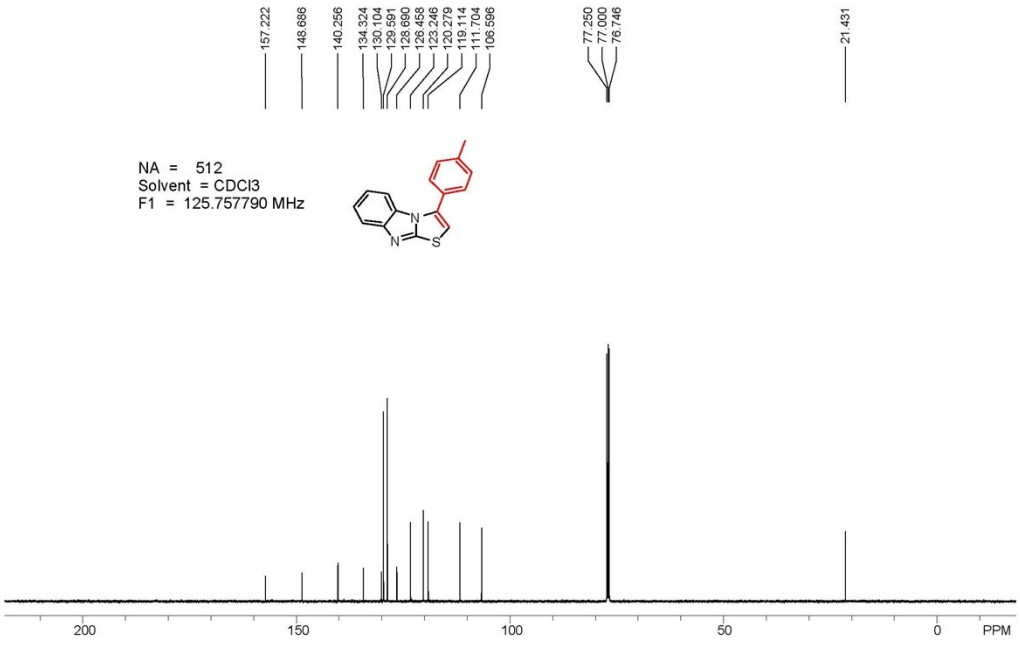

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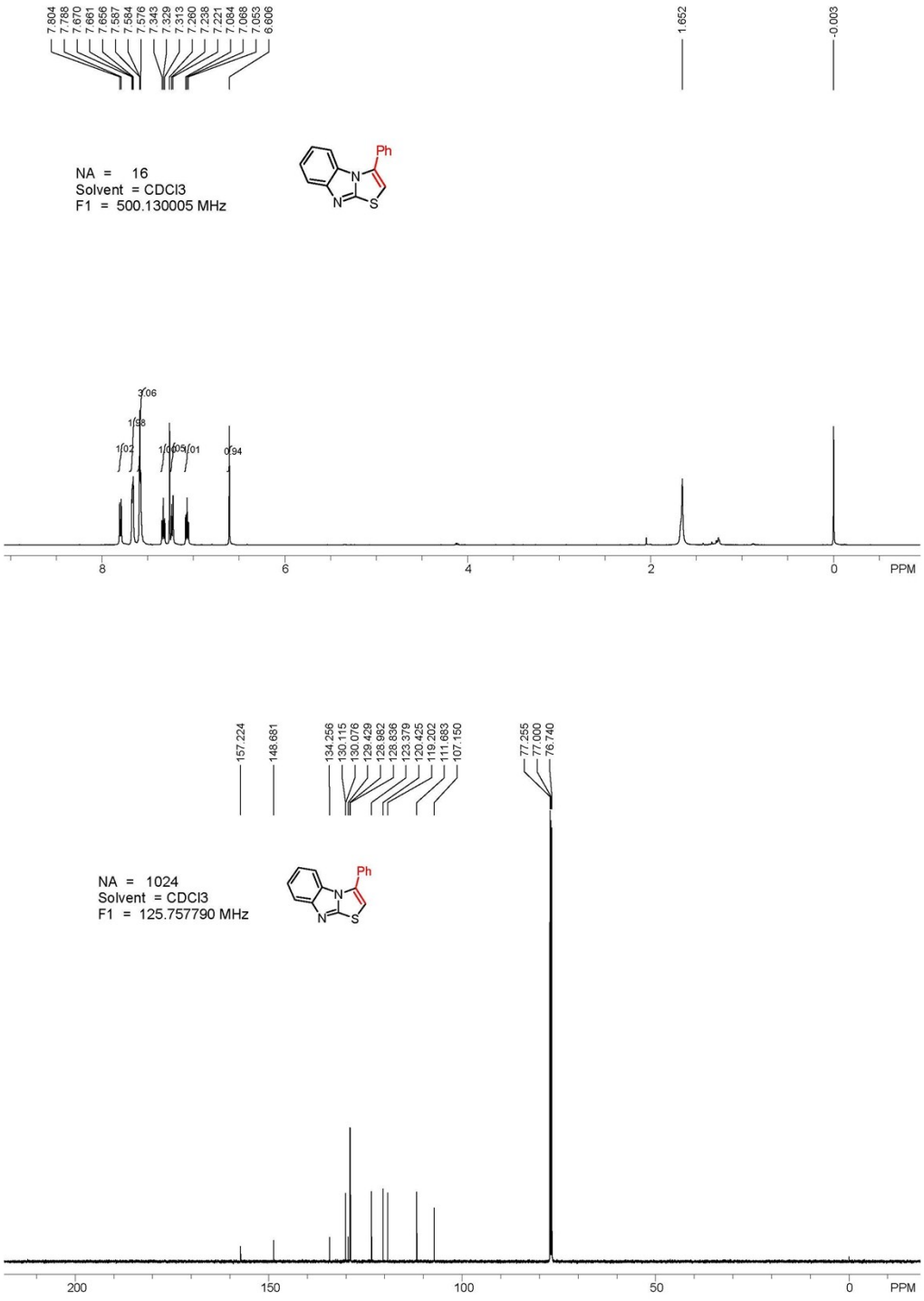
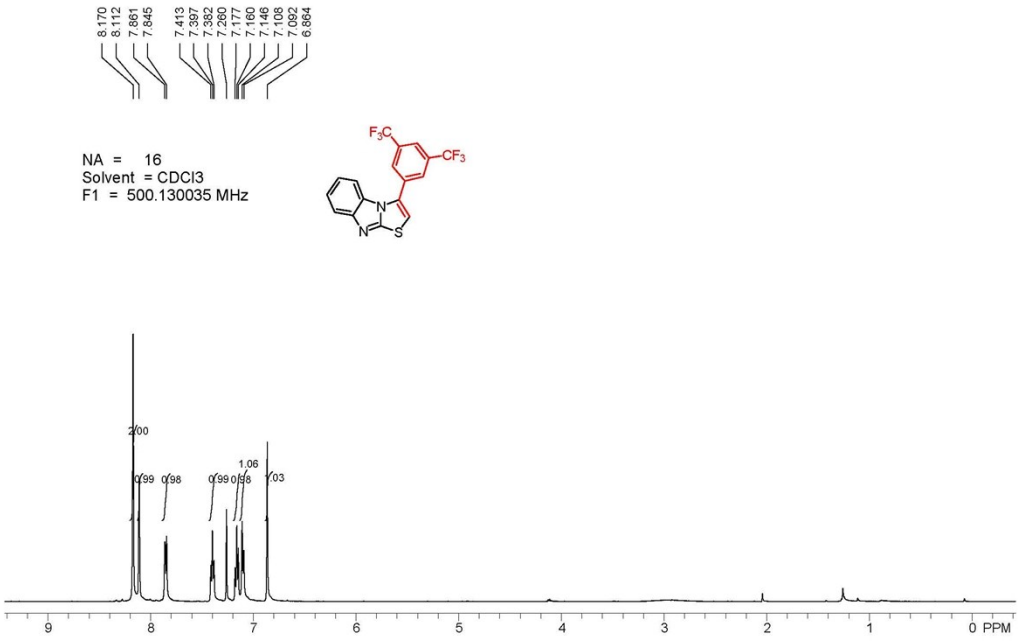
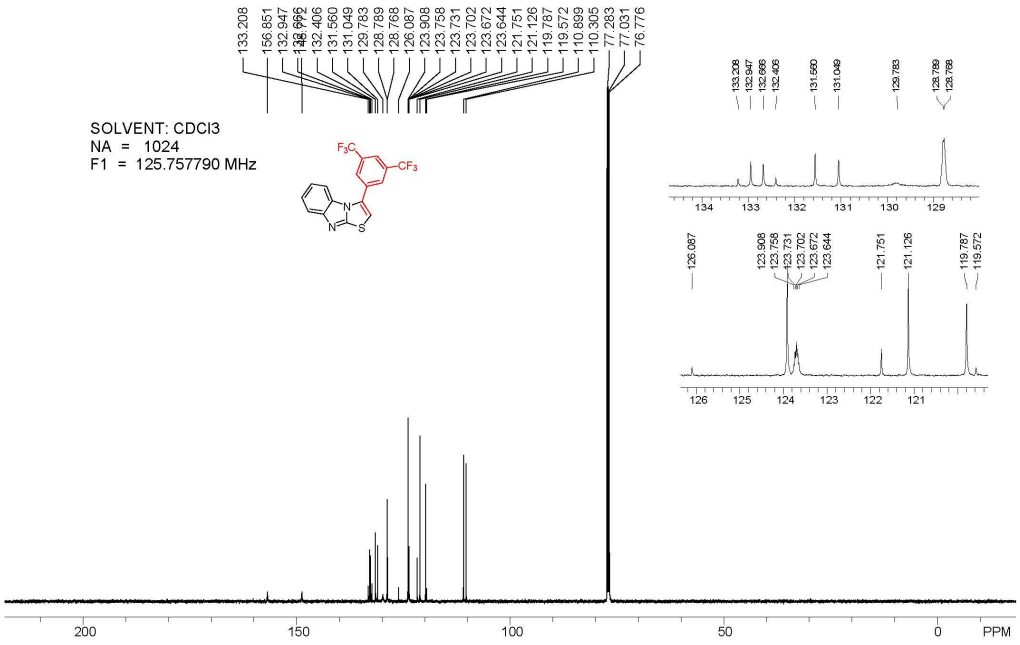
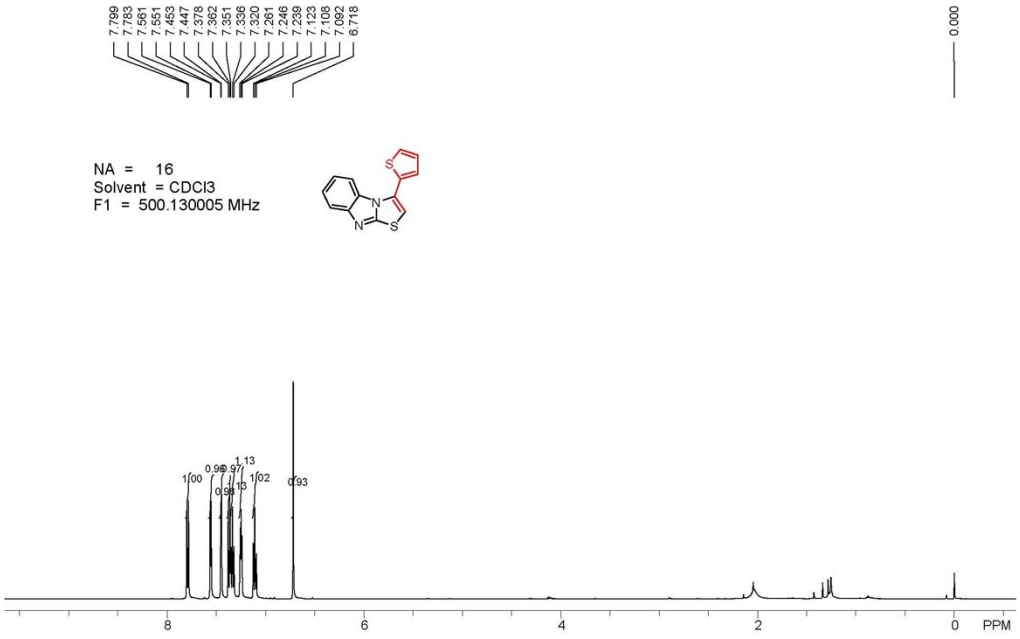


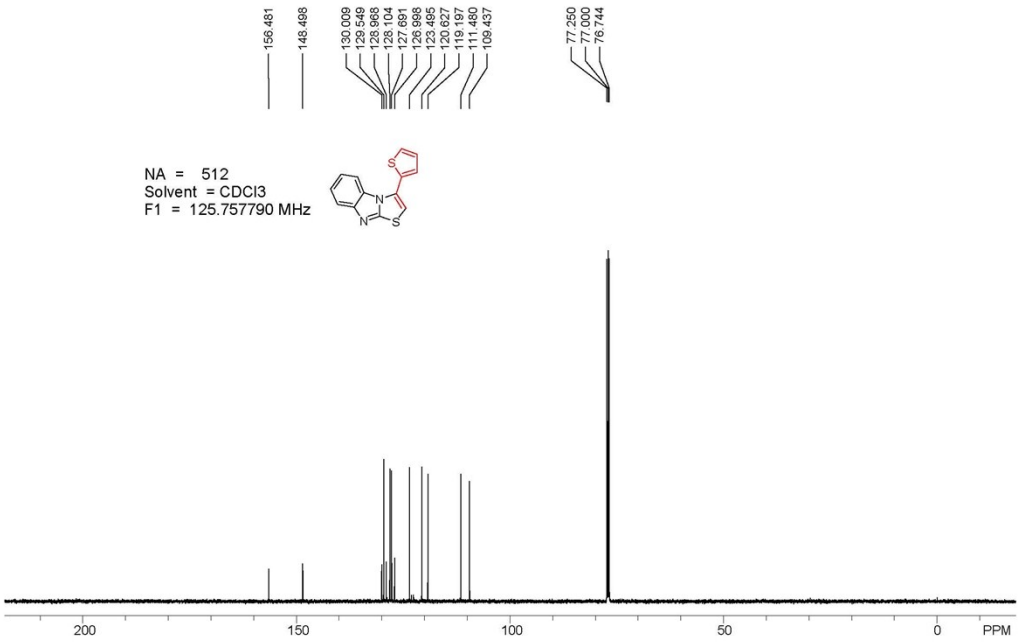
3-(3,5-Bis(trifluoromethyl)phenyl)thiazolo[3,2-a]benzimidazole (3ka)



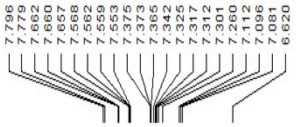


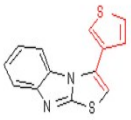
3-Thiophen-2-ylthiazolo[3,2-a]benzimidazole (3la)





3-Thiophen-2-ylthiazolo[3,2-a]benzimidazole (3ma)





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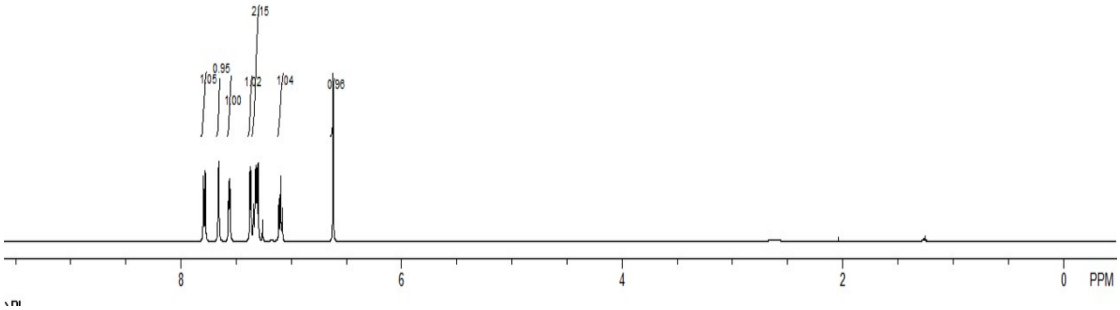

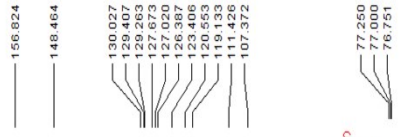

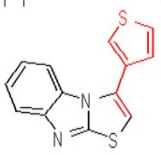

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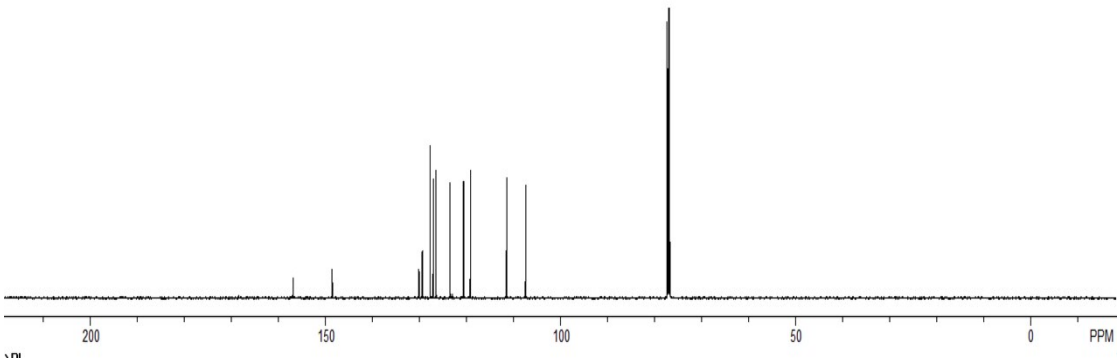
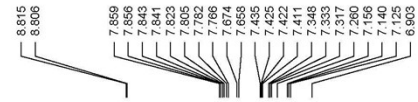


3-Pyridin-2-ylthiazolo[3,2-a]benzimidazole (3na)



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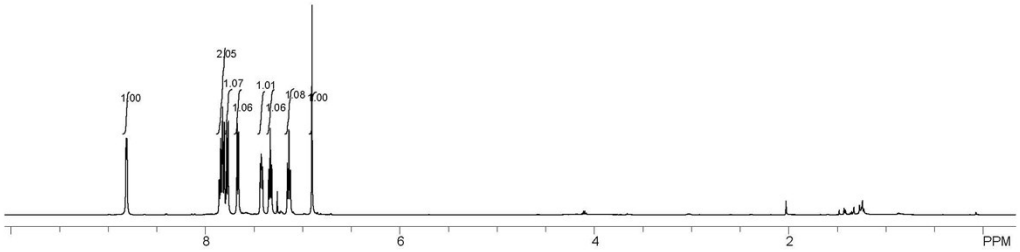

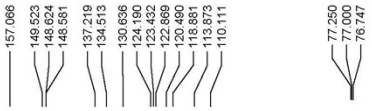

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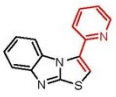
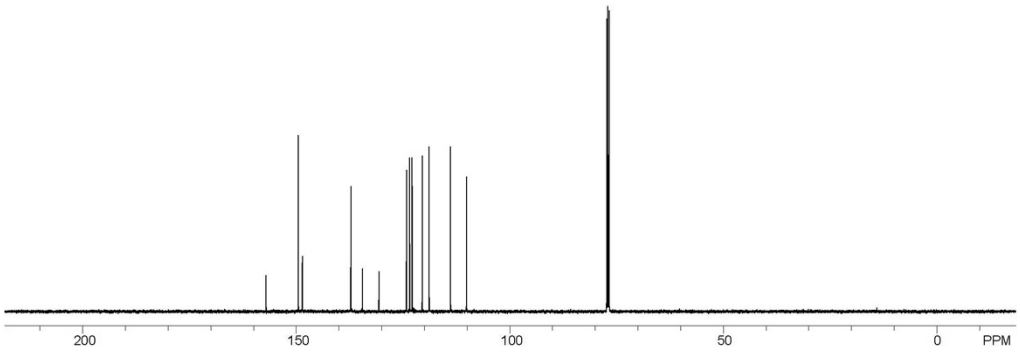
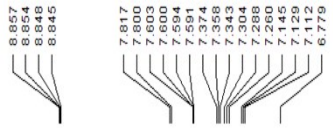




3-Pyridin-4-ylthiazolo[3,2-a]benzimidazole (3oa)



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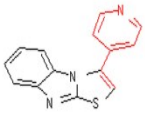

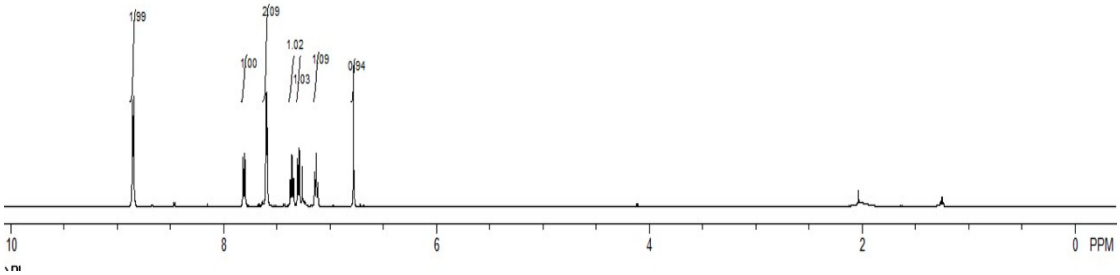

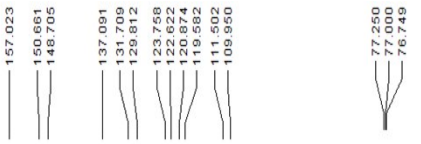

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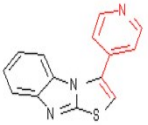
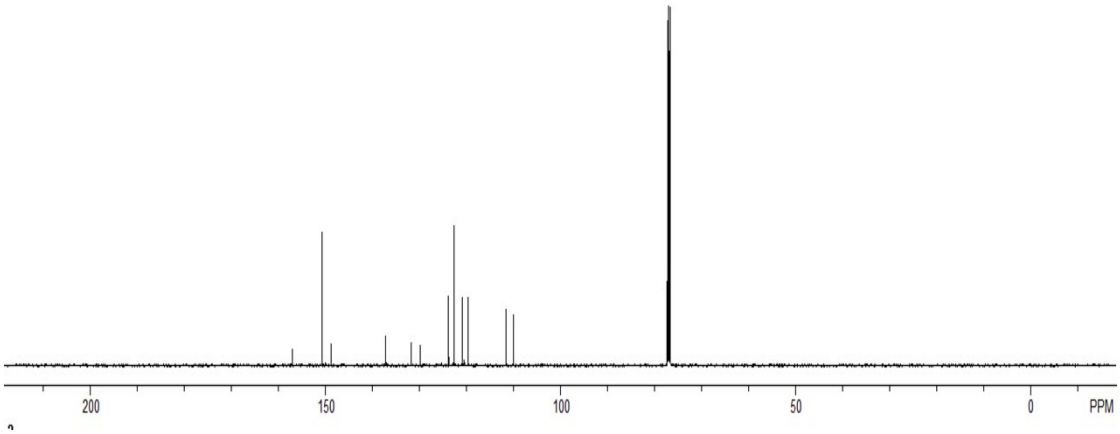
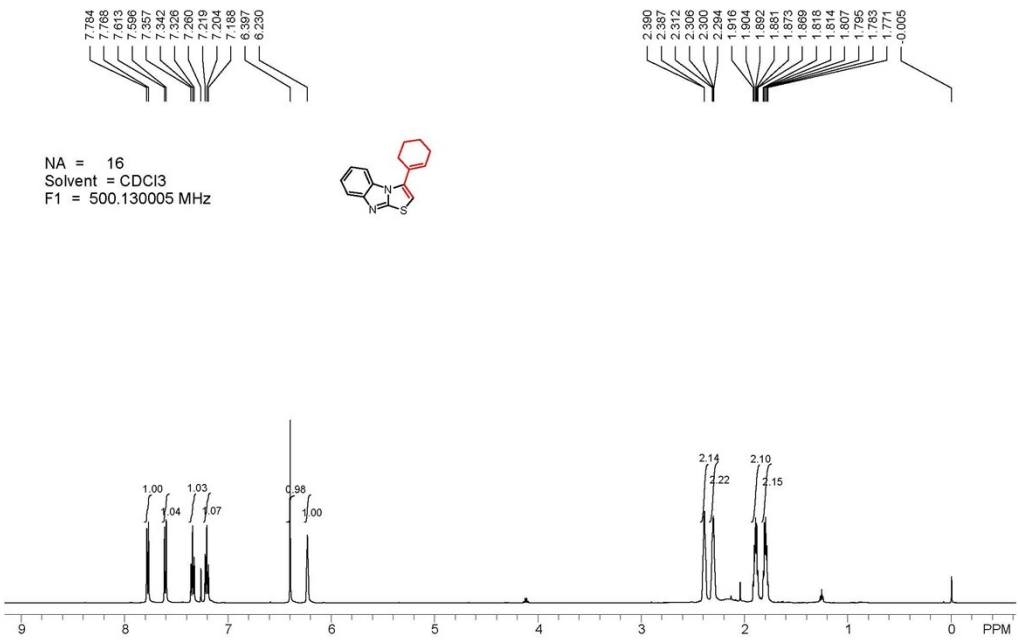
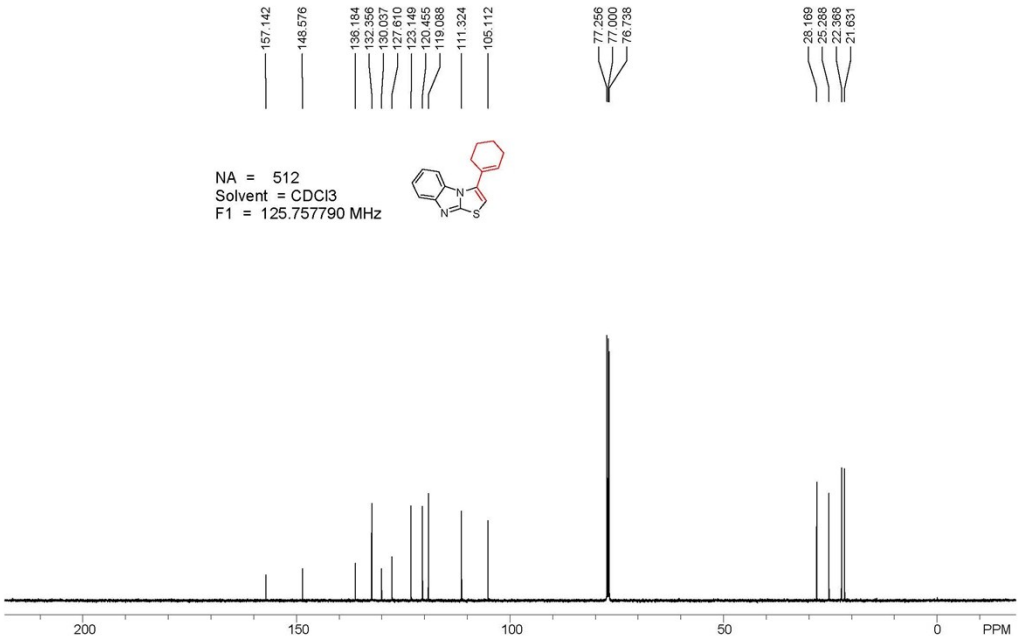


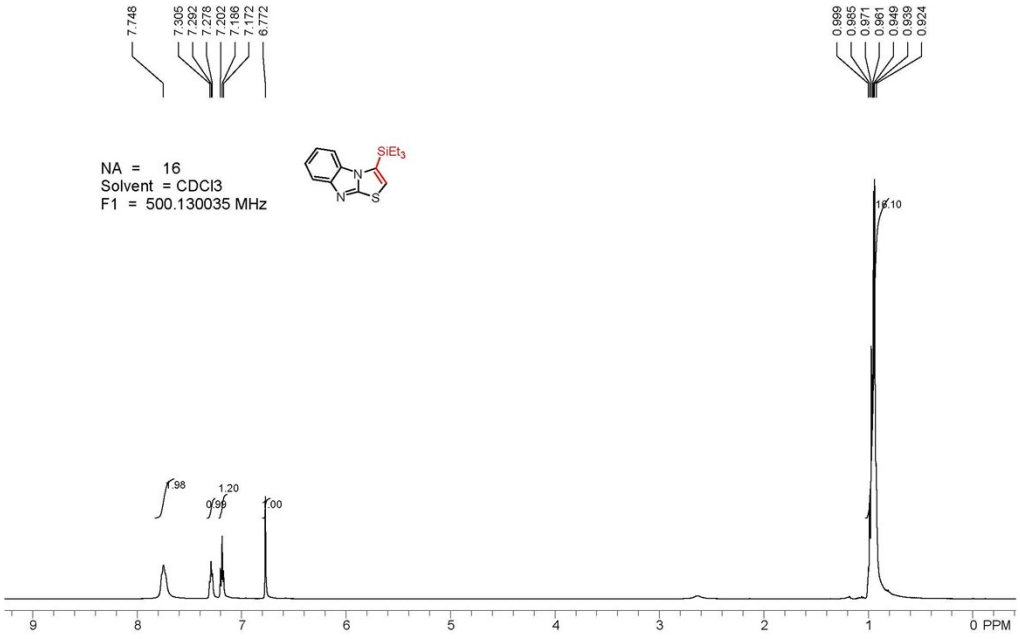


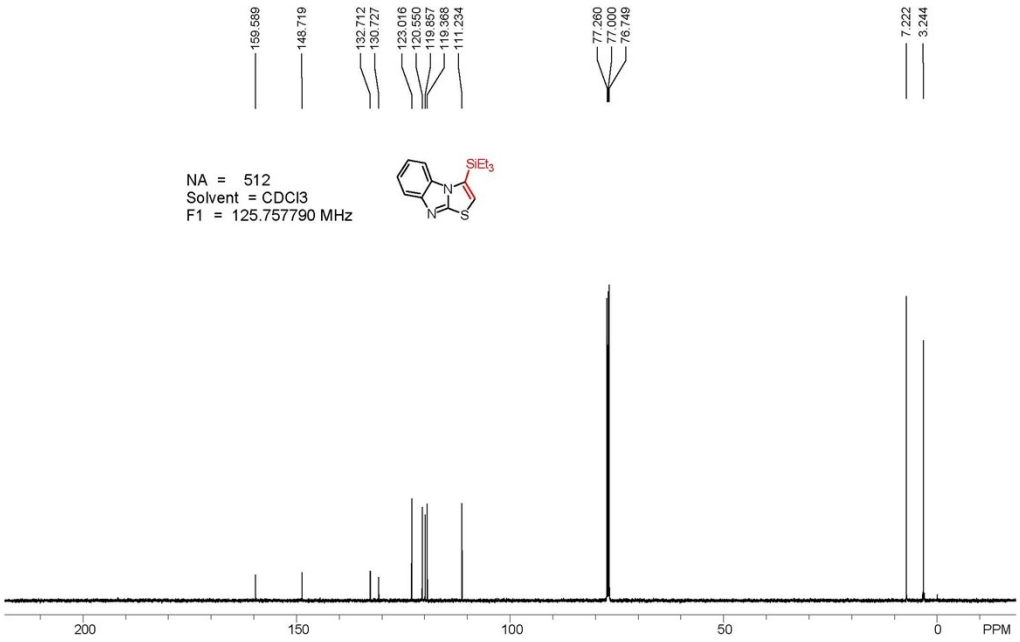
3-(Cyclohexen-1-yl)thiazolo[3,2-a]benzimidazole (3pa)



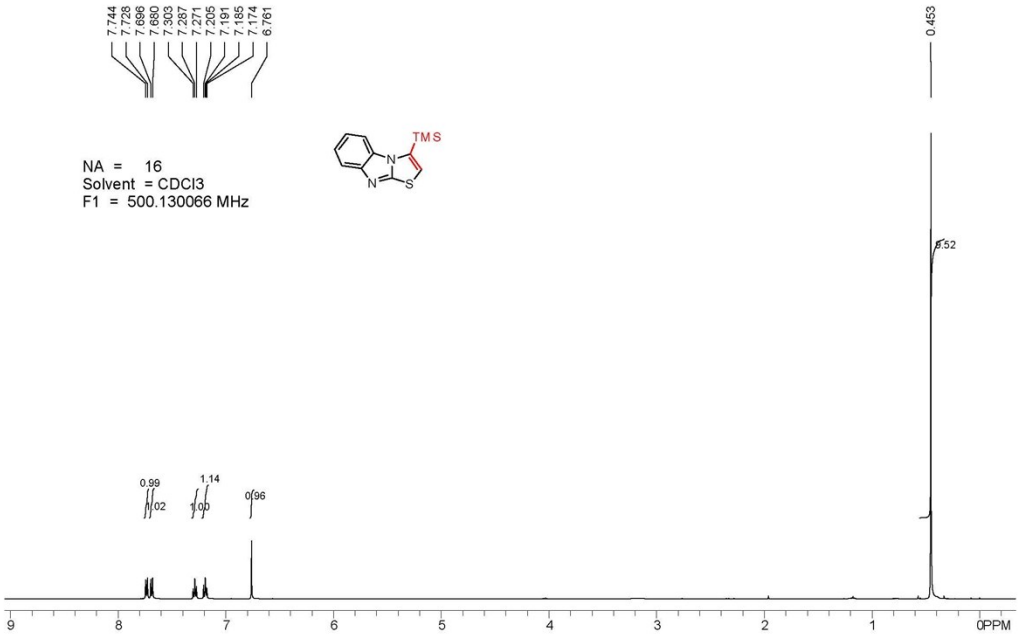


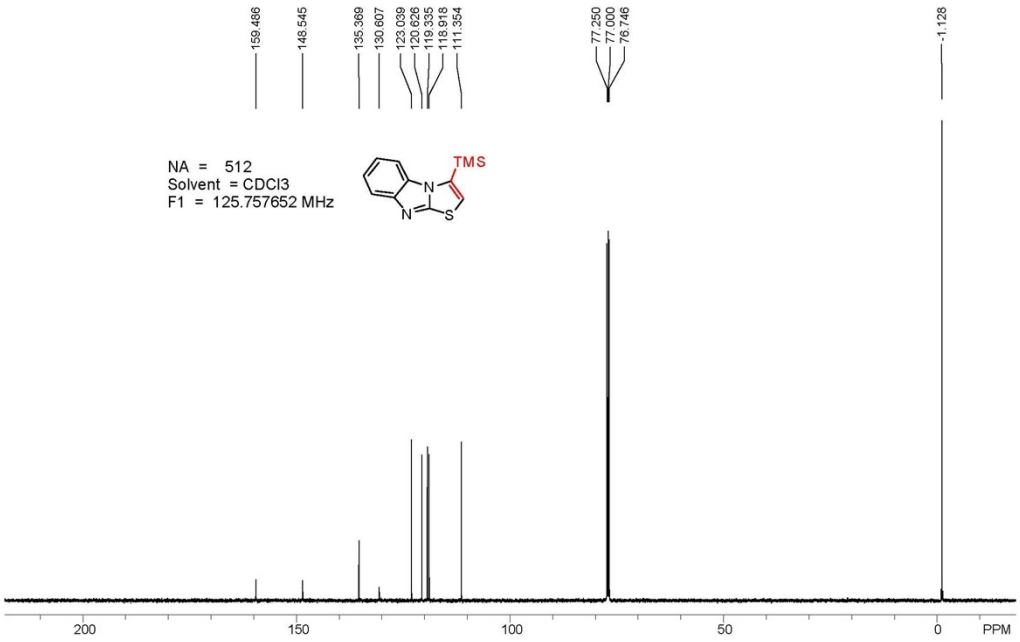
3-(Triethylsilyl)thiazolo[3,2-a]benzimidazole (3qa)



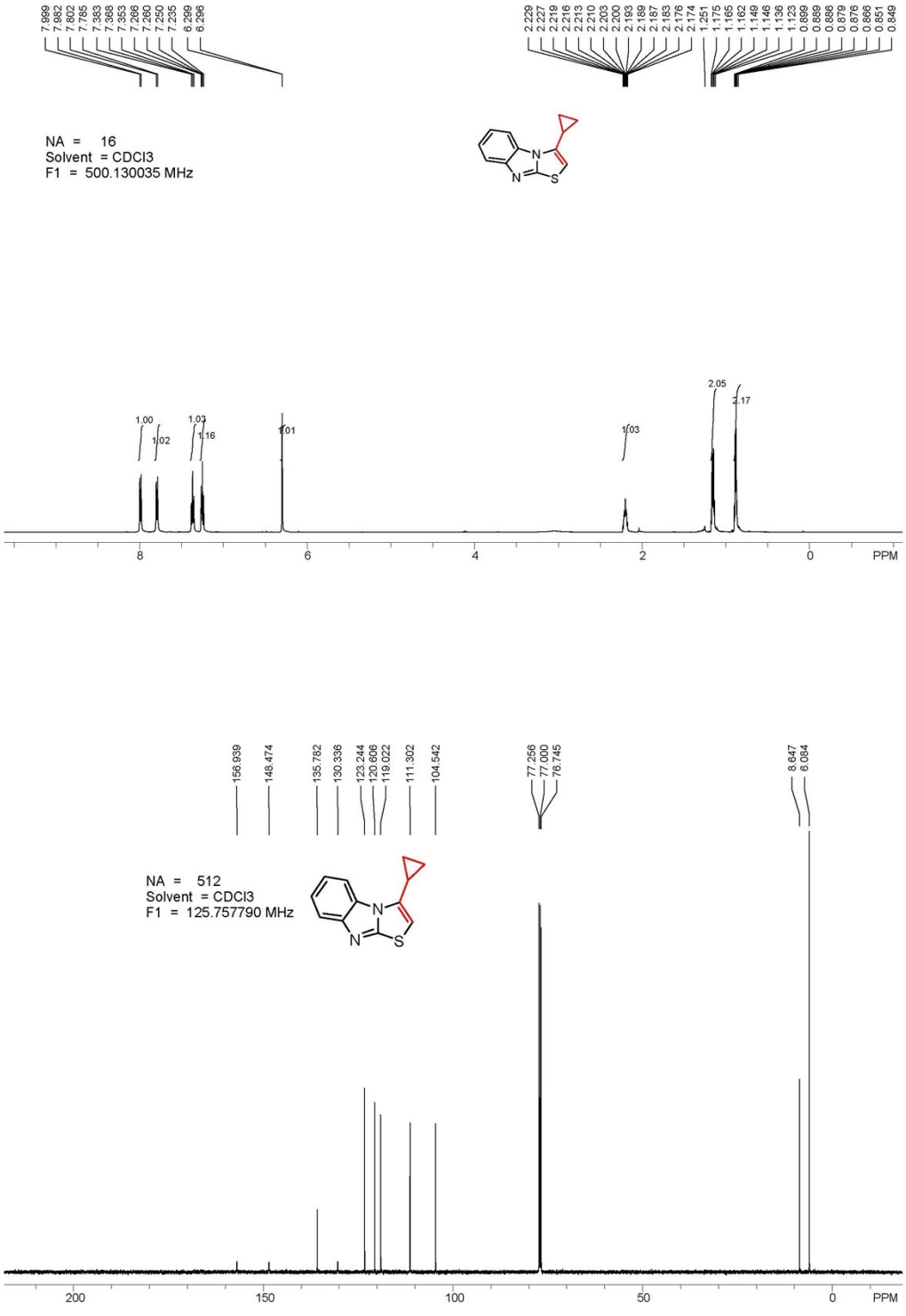


3-(Trimethylsilyl)thiazolo[3,2-a]benzimidazole (3ra)

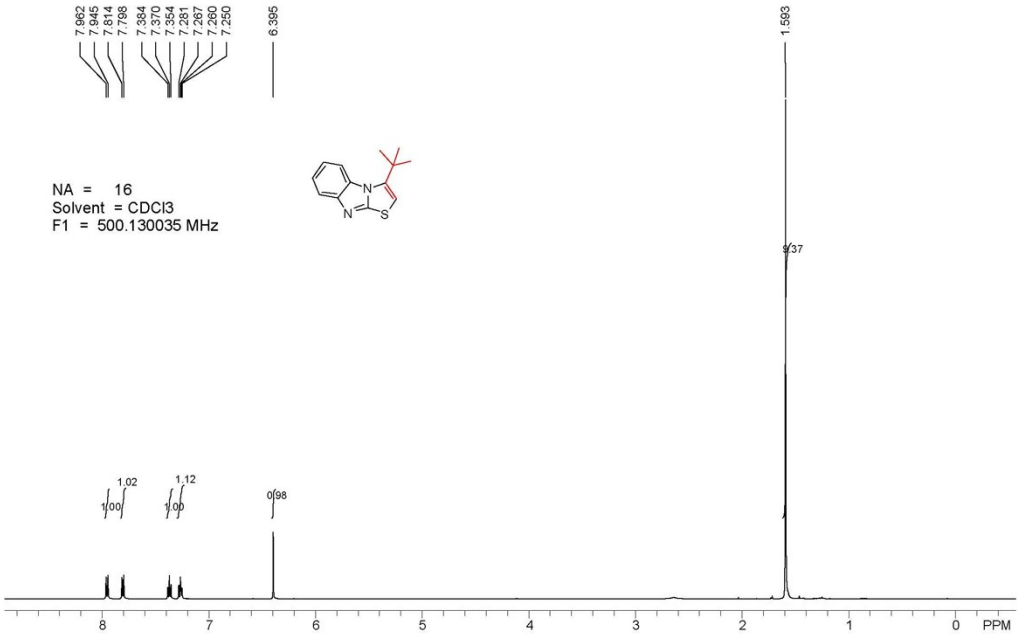


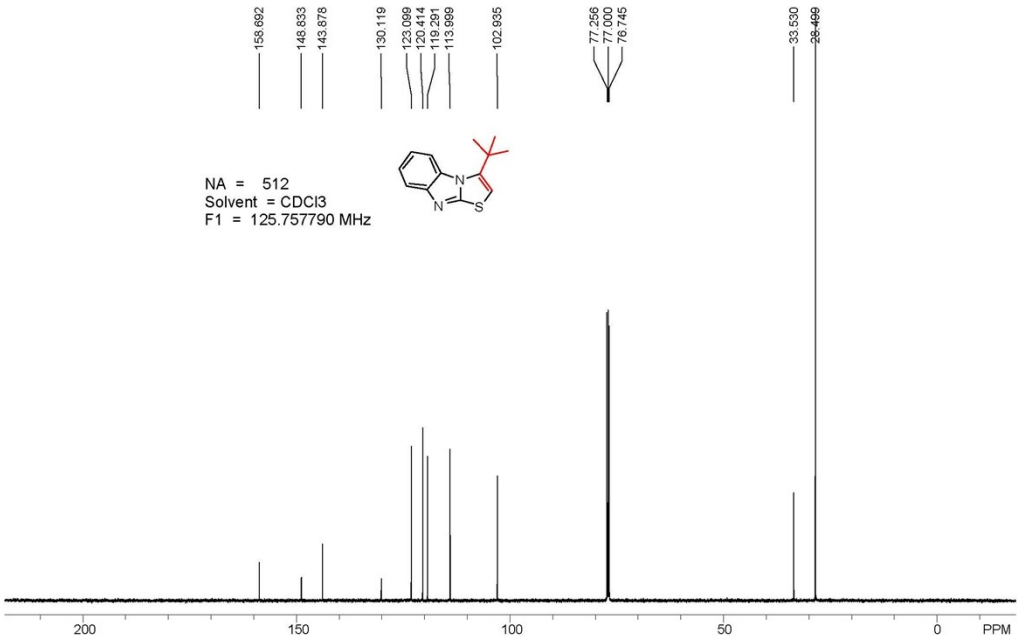


3-(Cyclopropyl)thiazolo[3,2-a]benzimidazole (3sa)

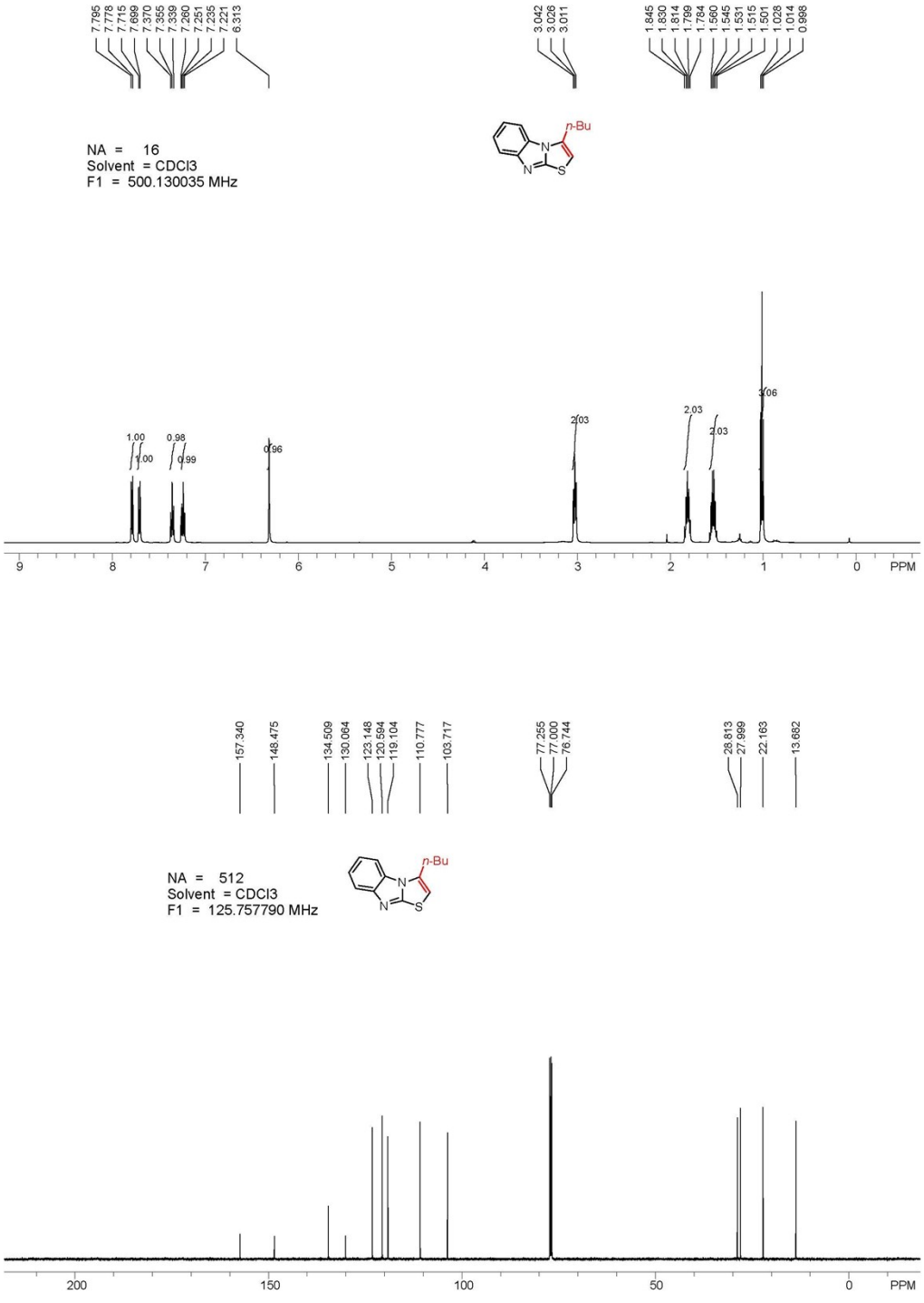


3-*tert*-Butylthiazolo[3,2-a]benzimidazole (3ta)

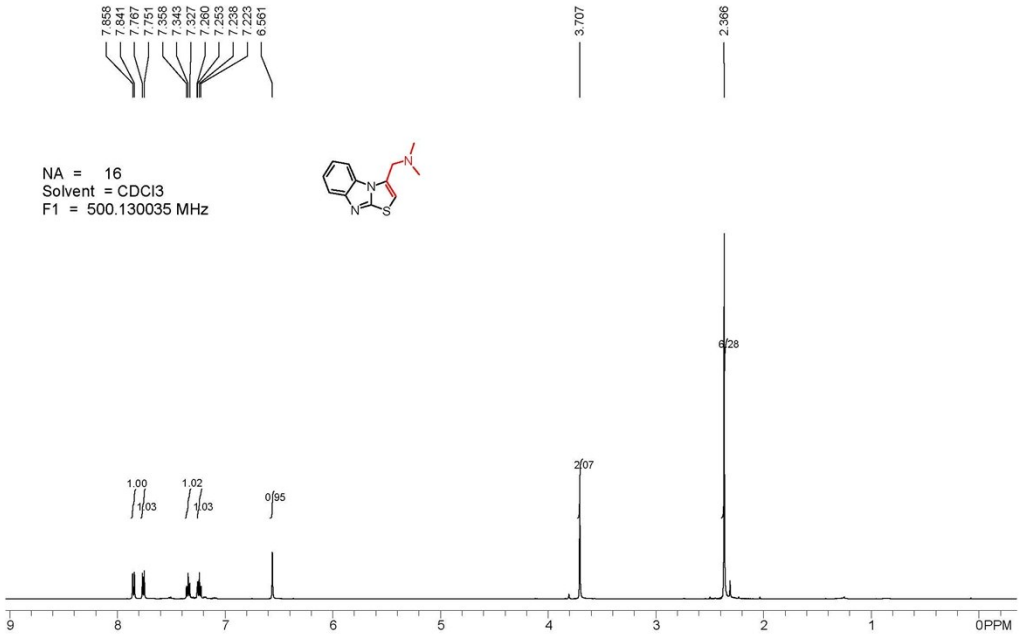


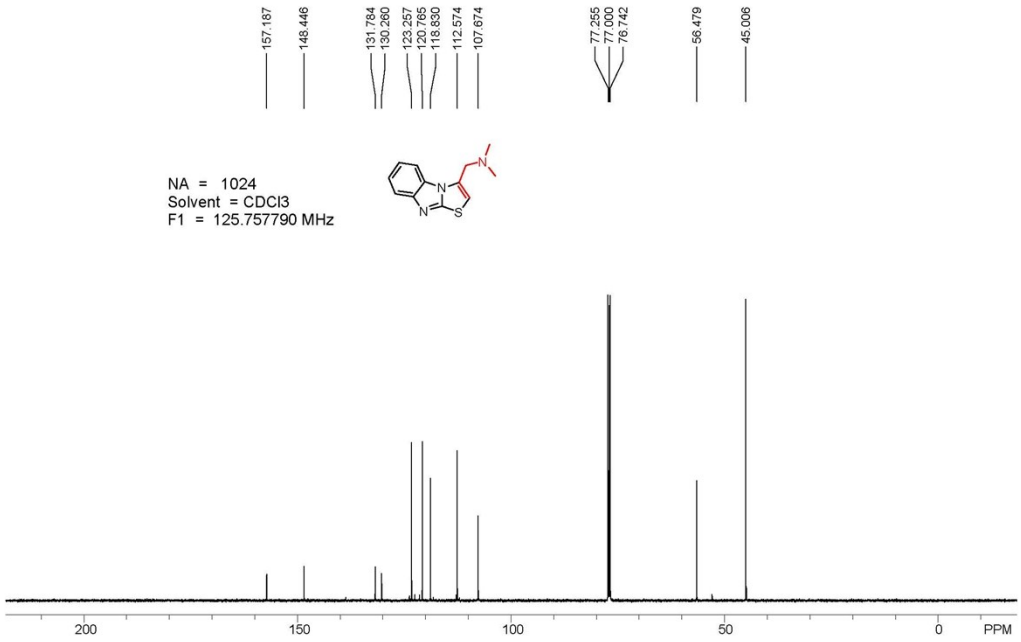


3-Butylthiazolo[3,2-a]benzimidazole (3ua)

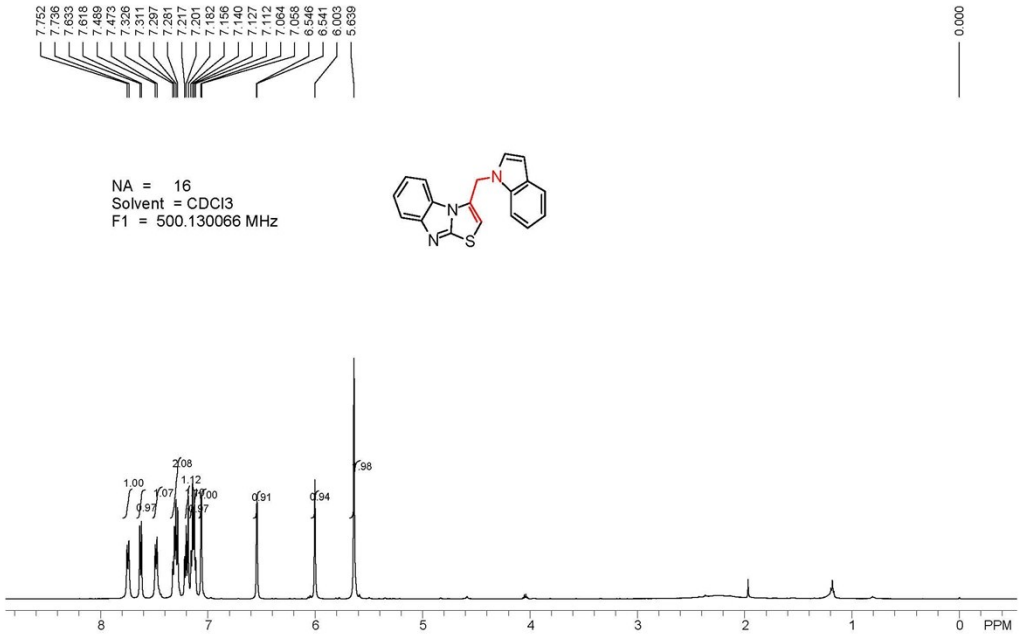


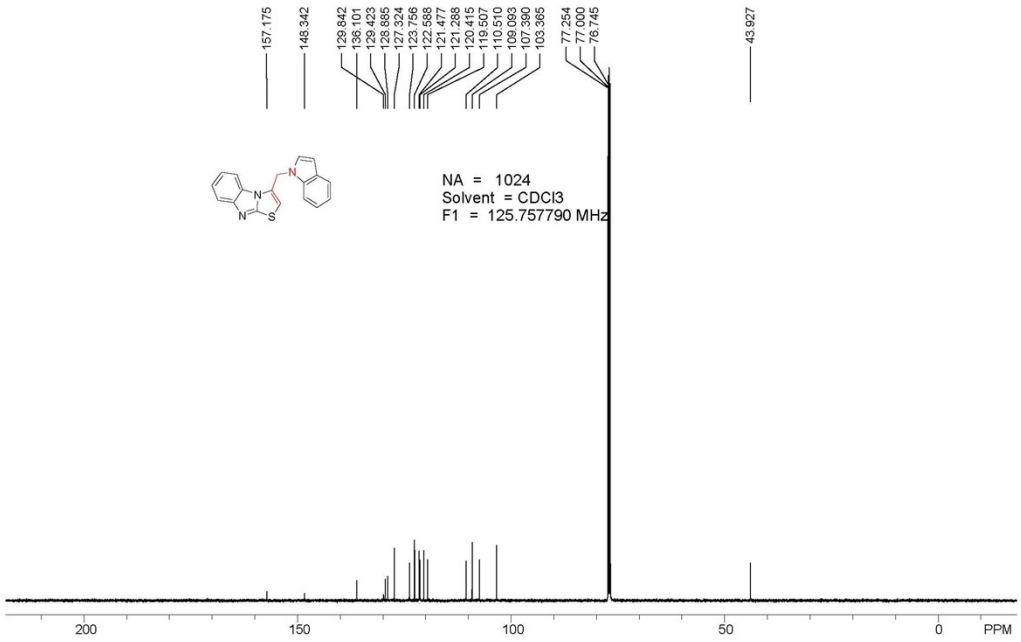
N,N-Dimethylthiazolo[3,2-a]benzimidazol-3-yl-methanamine (3va)



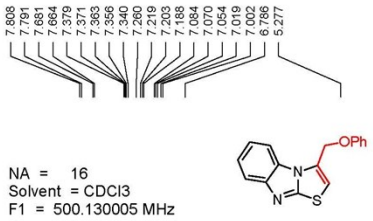


3-((1H-Indol-1-yl)methyl)thiazolo[3,2-a]benzimidazole (3wa)





3-Phenoxymethylthiazolo[3,2-a]benzimidazole (3xa)



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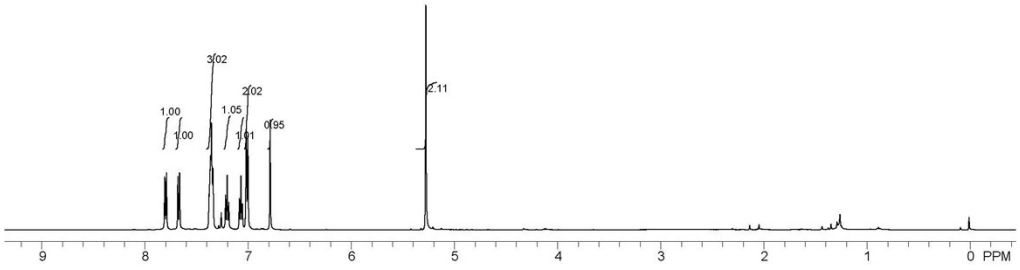
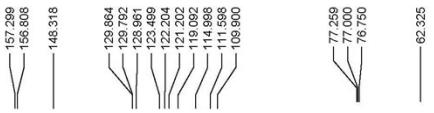
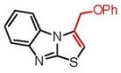
F1 = 500.130005 MHz







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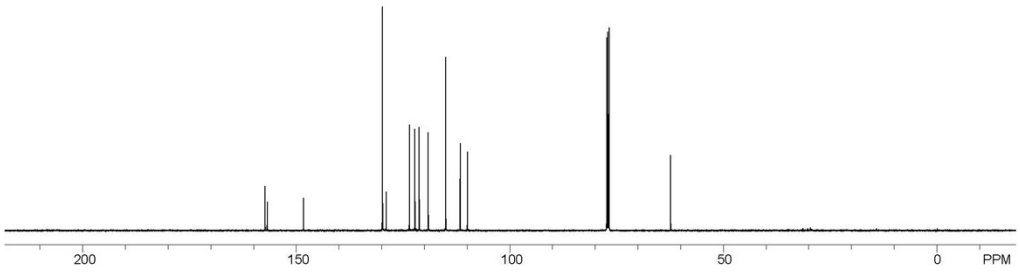
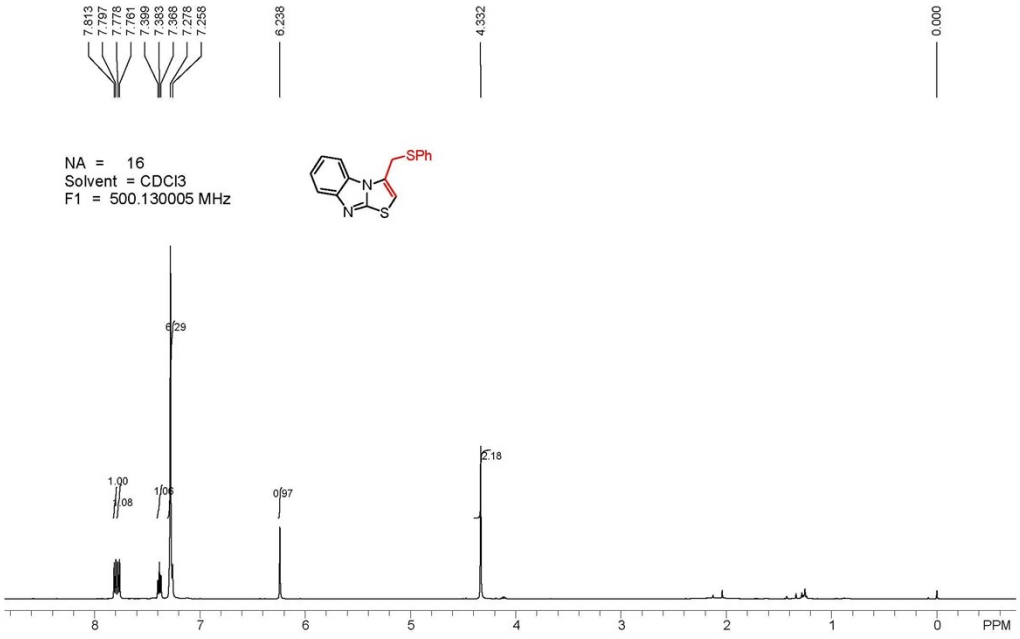
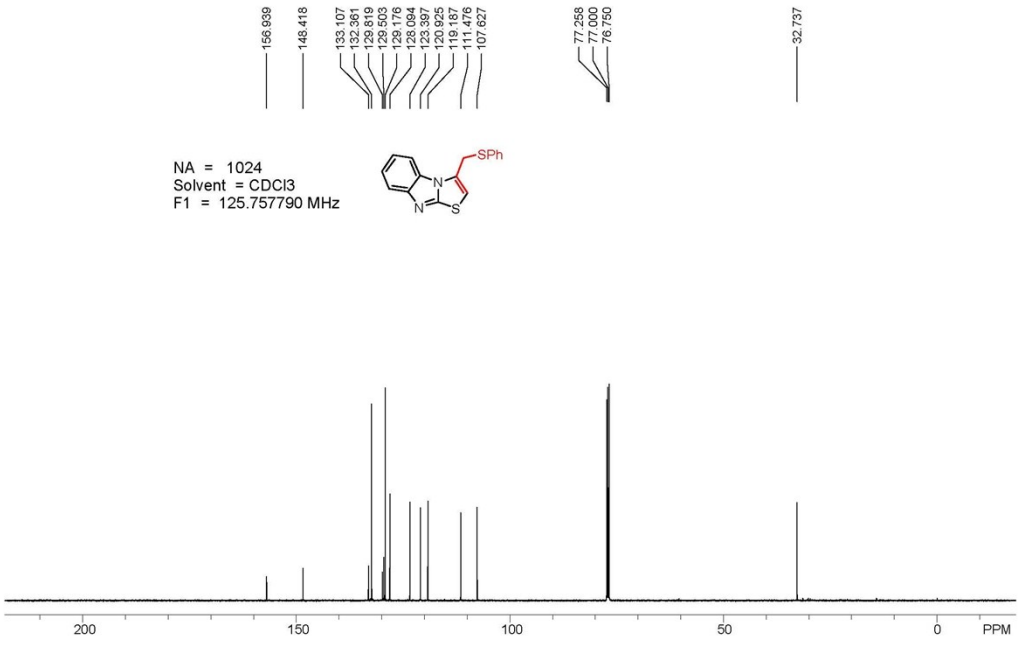
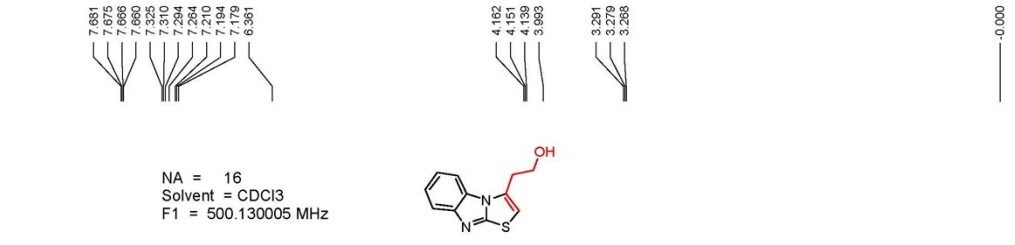


3-Phenylthiomethylthiazolo[3,2-a]benzimidazole (3ya)





Thiazolo[3,2-*a*]benzimidazol-3-yl-ethanol (3za)



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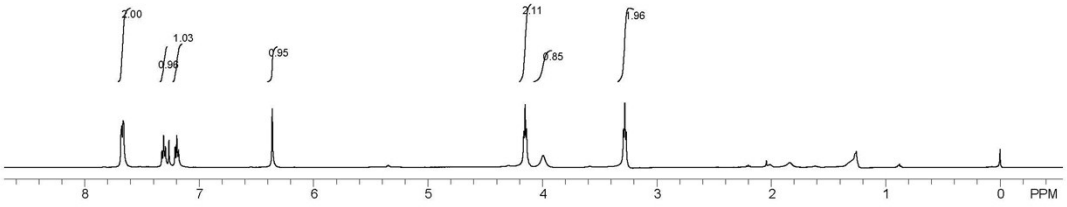

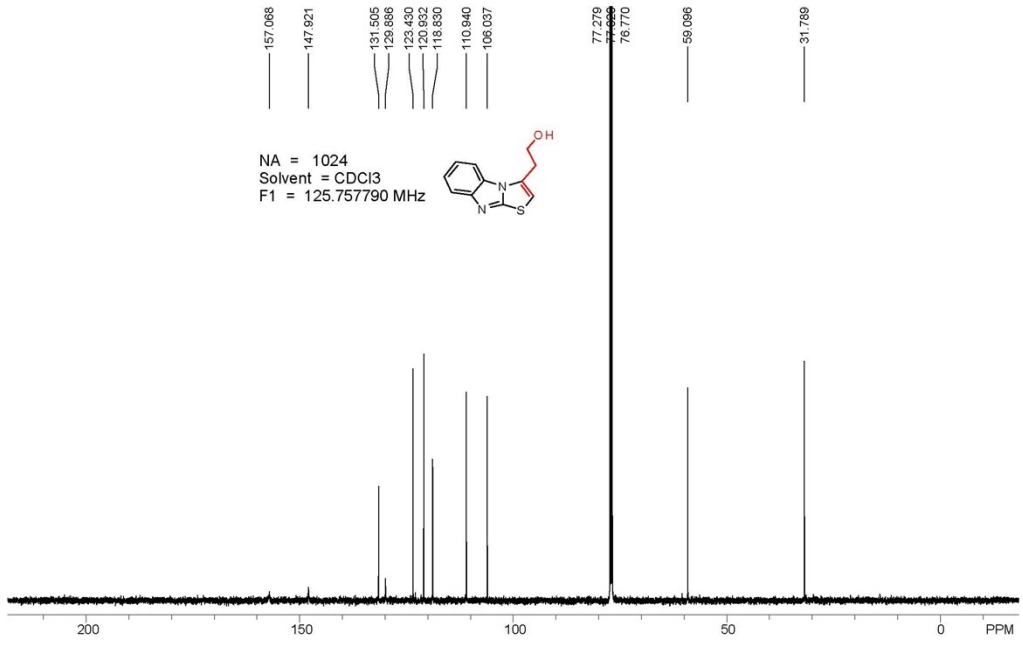

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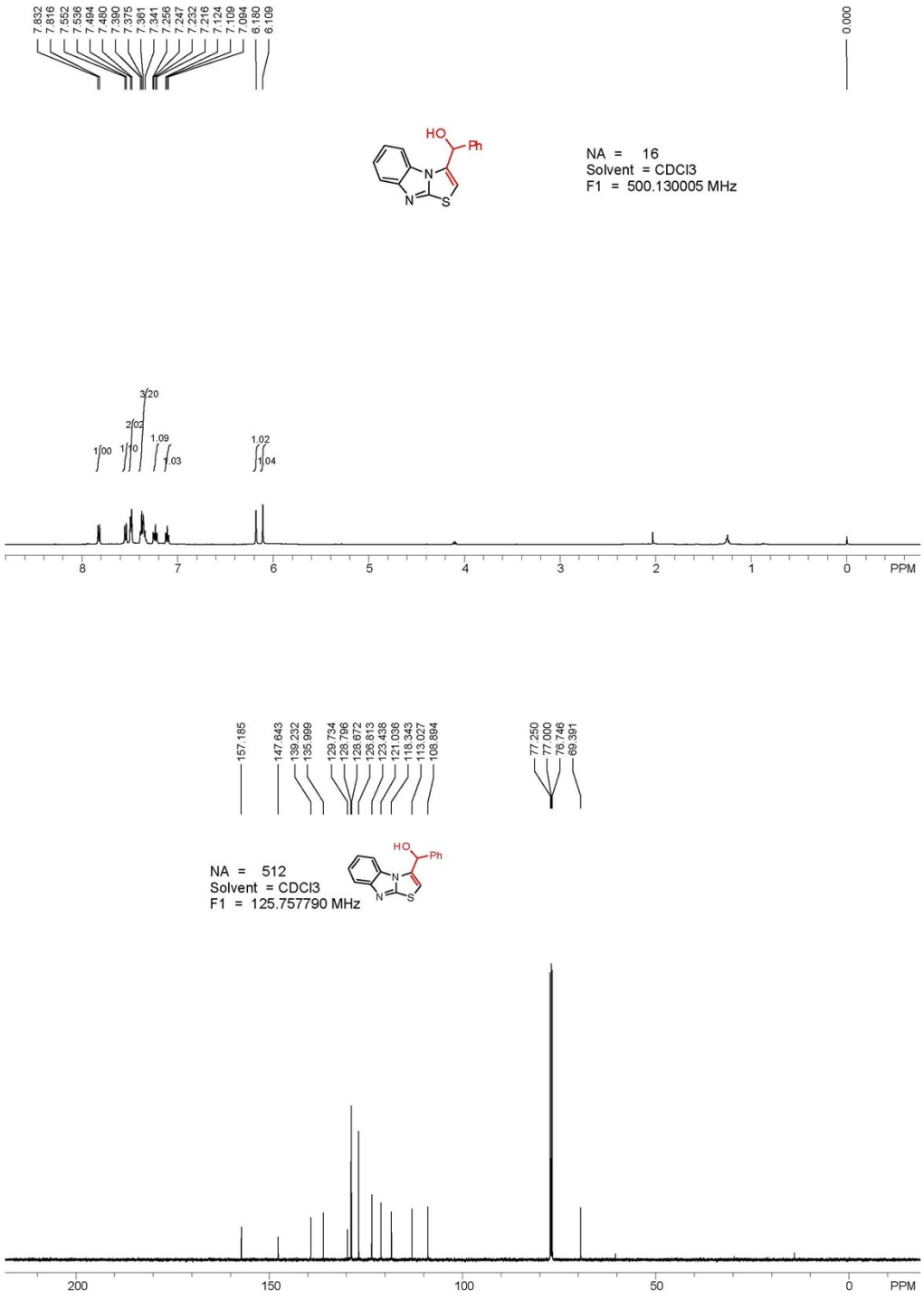
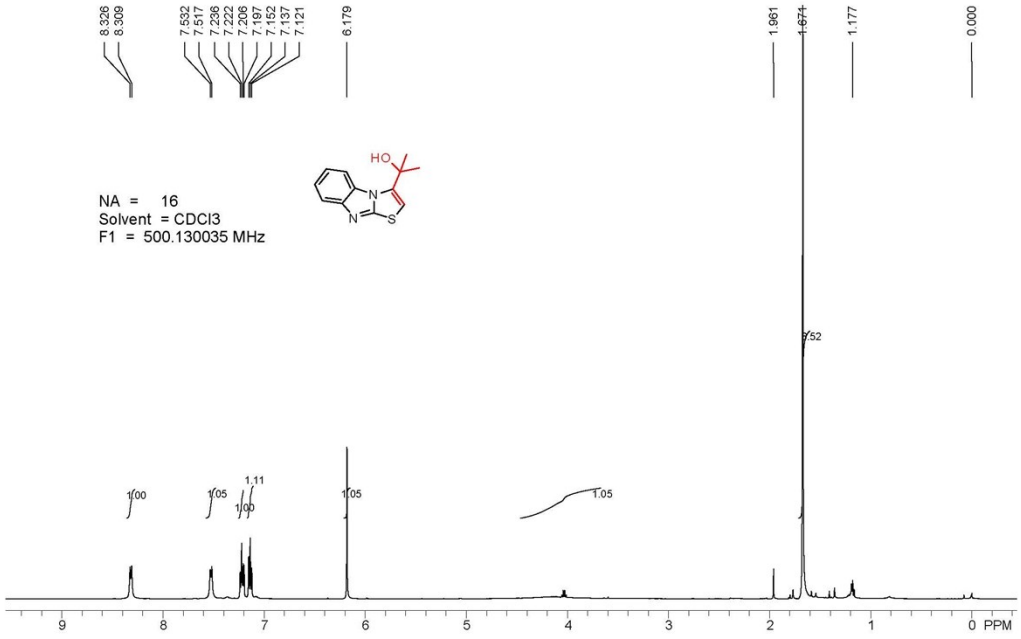
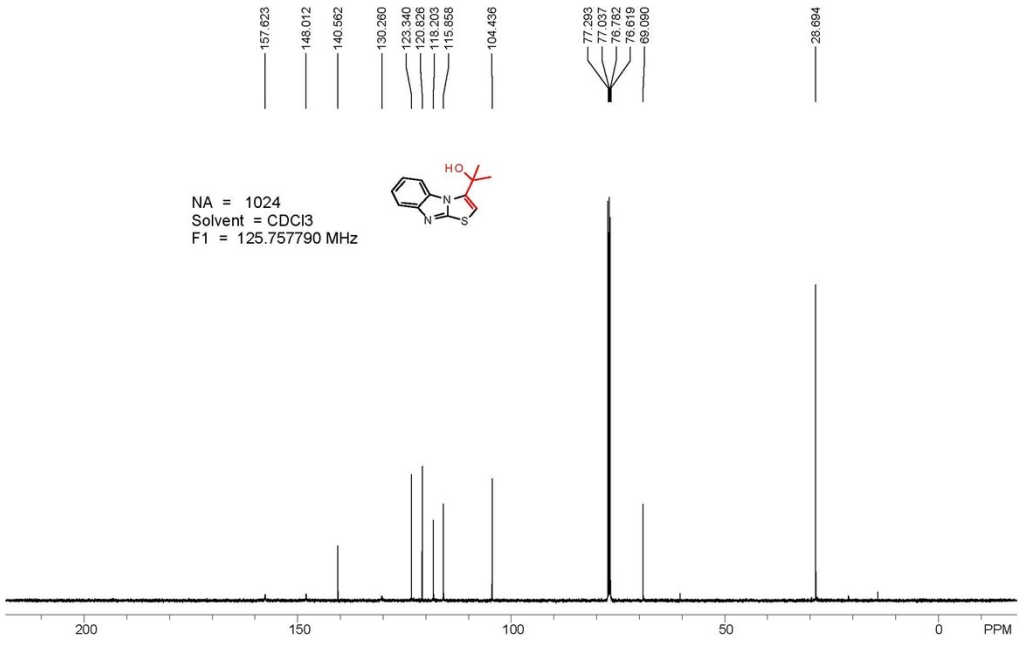
Thiazolo[3,2-*a*]benzimidazol-3-yl-(phenyl)methanol (3Aa)

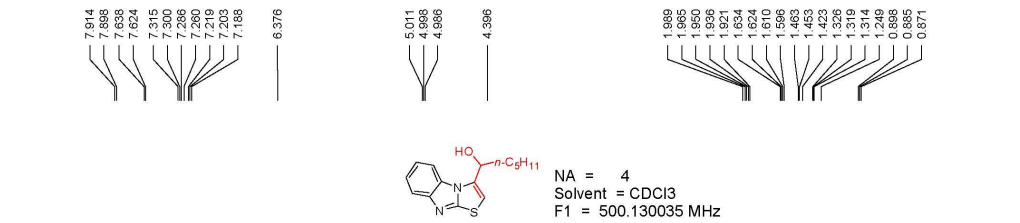


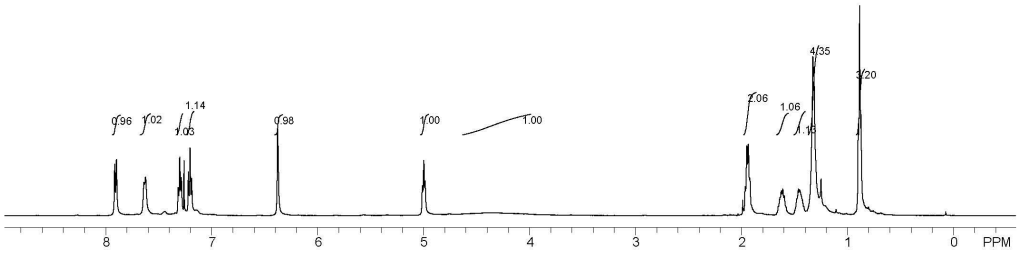
Thiazolo[3,2-*a*]benzimidazol-3-yl-propan-2-ol (3Ba)

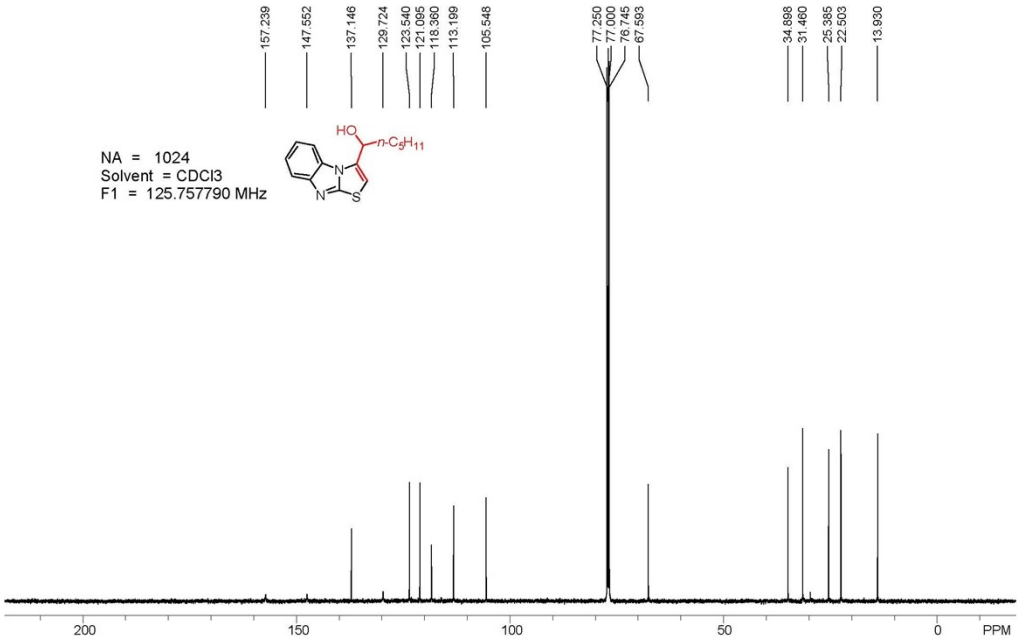




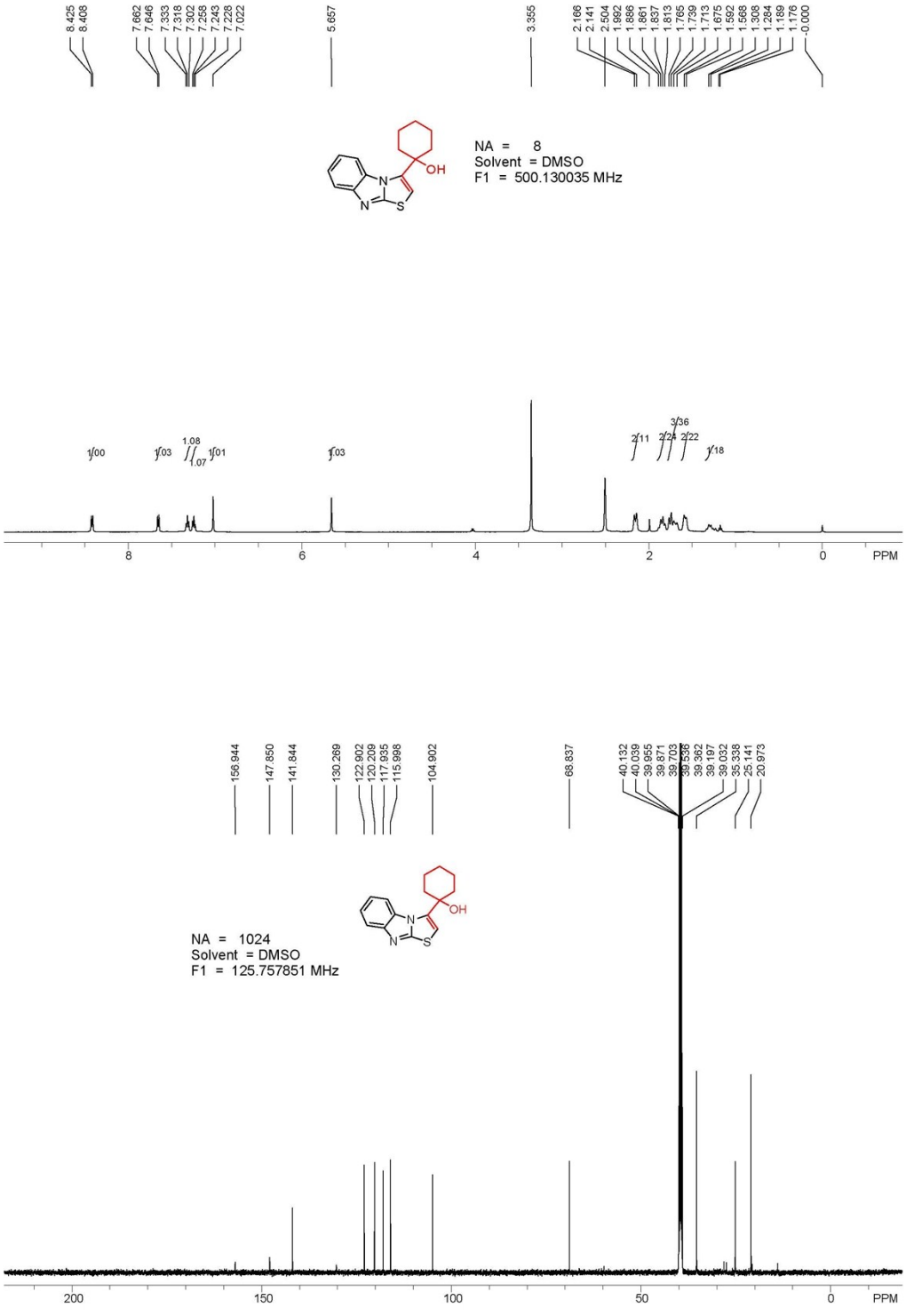
Thiazolo[3,2-*a*]benzimidazol-3-yl-hexan-1-ol (3Ca)



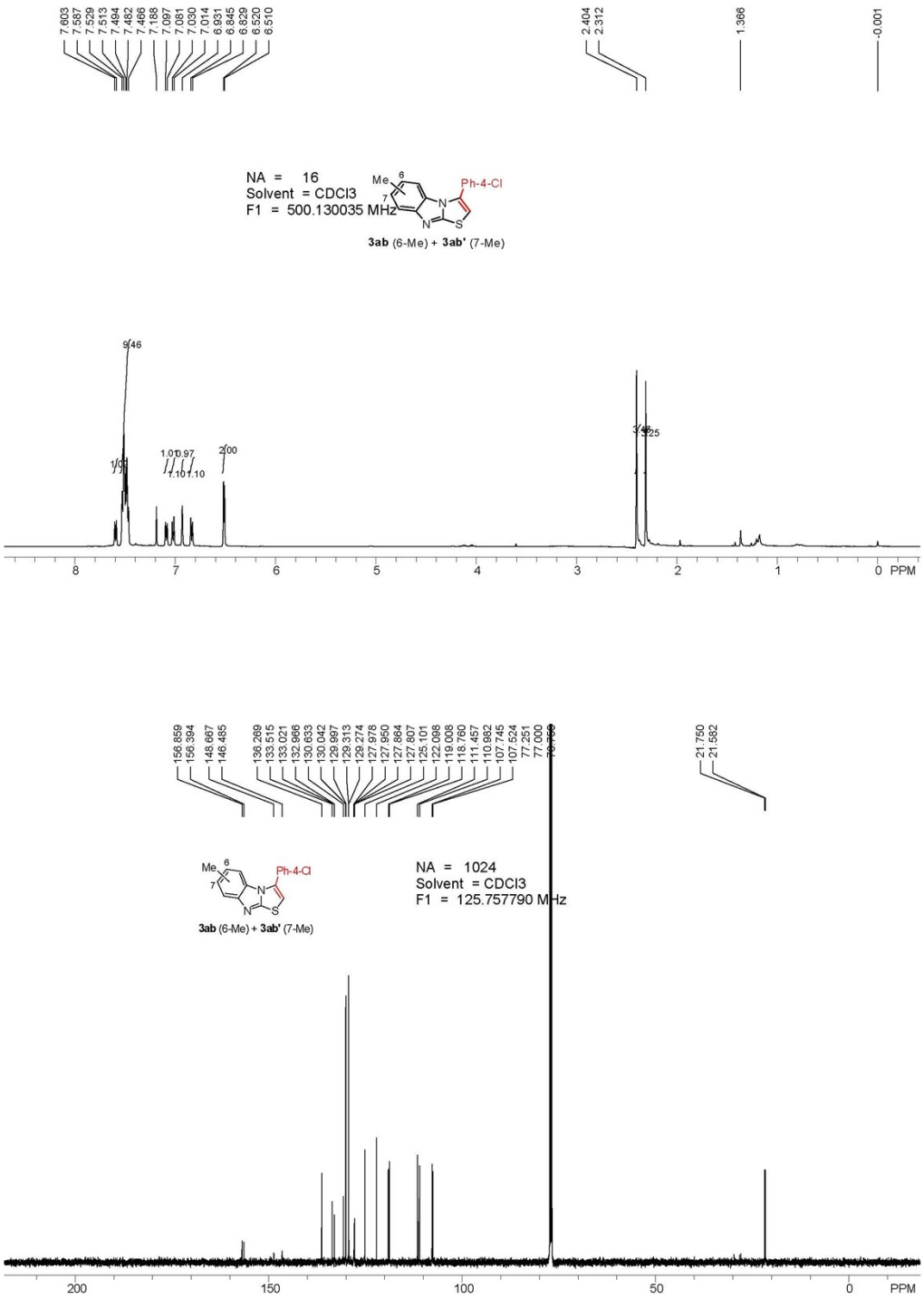




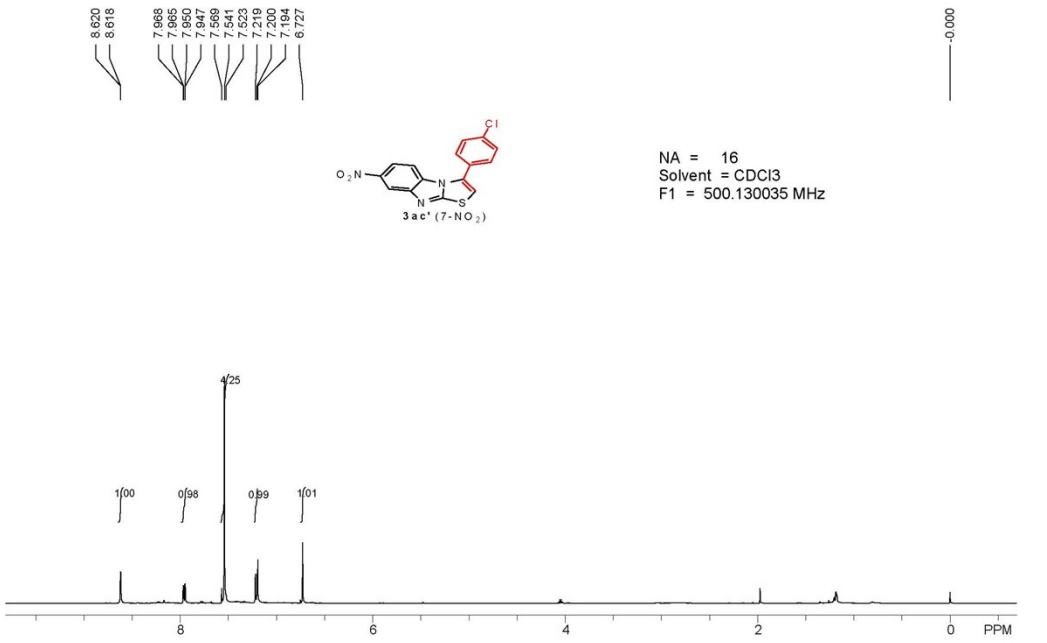
Thiazolo[3,2-*a*]benzimidazol-3-yl-cyclohexan-1-ol (3Da)

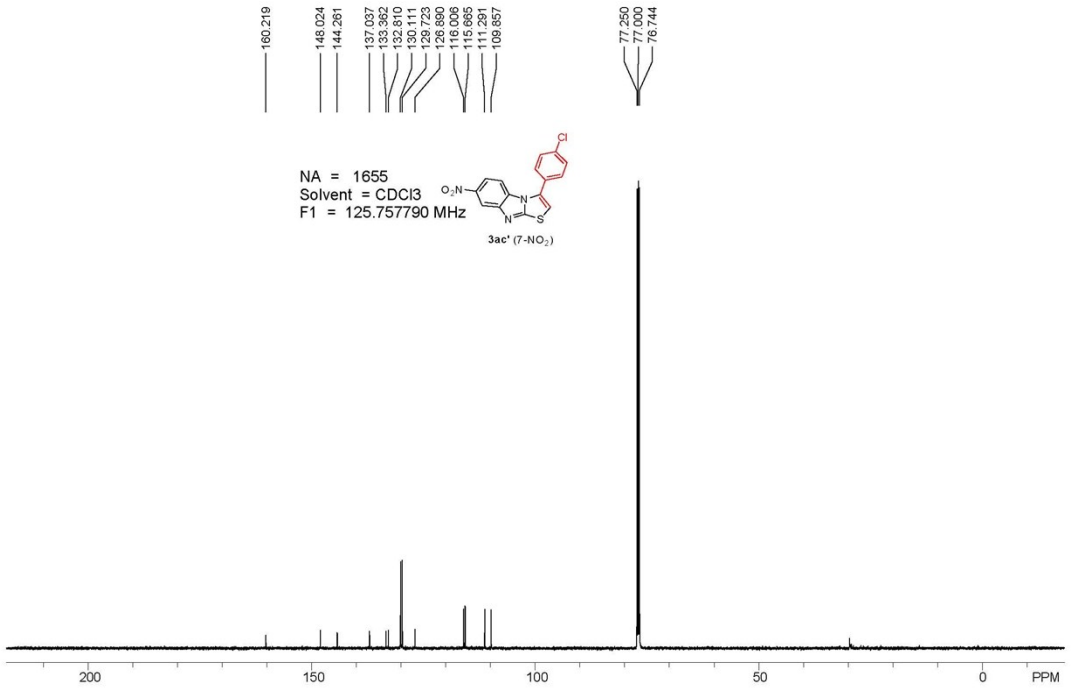


3-(4-Chlorophenyl)-6-methyl-thiazolo[3,2-a]benzimidazole (3ab) and 3-(4-Chlorophenyl)-7-methyl-thiazolo[3,2-a]benzimidazole (3ab')

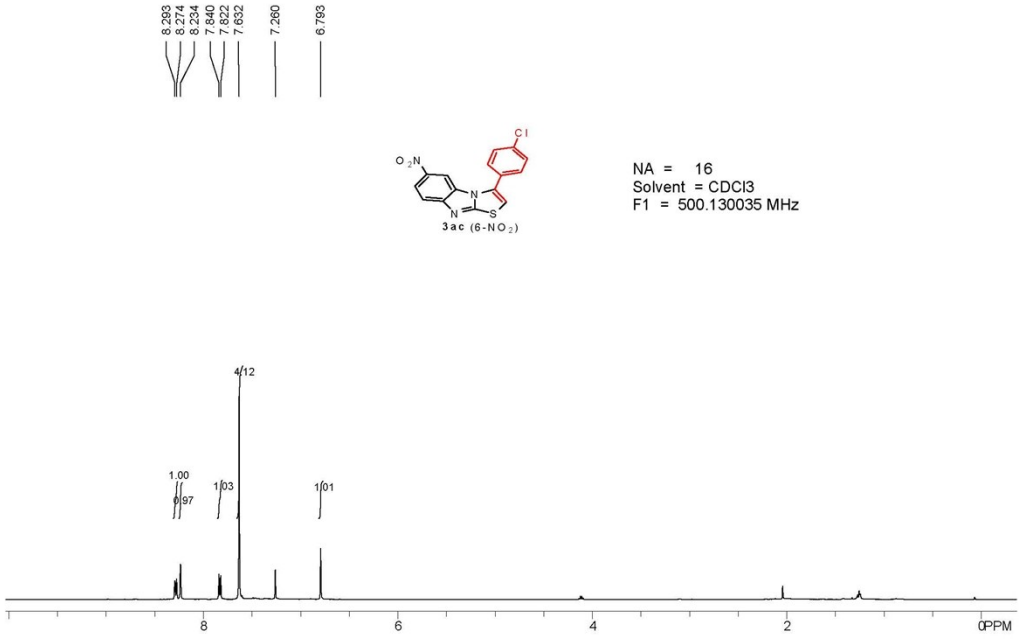


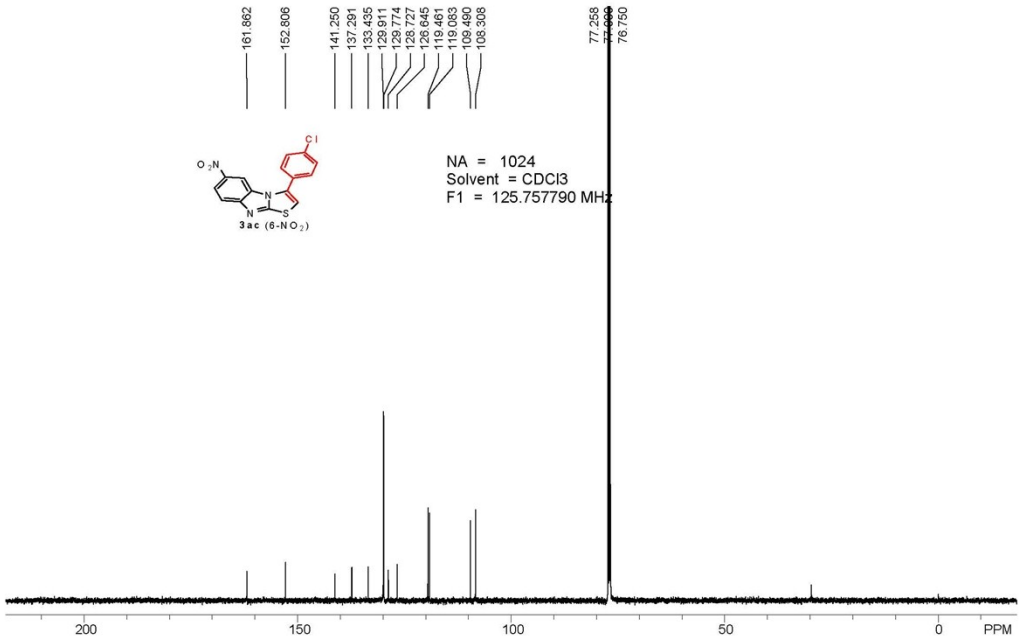
3-(4-Chlorophenyl)-7-nitro-thiazolo[3,2-a]benzimidazole (3ac')



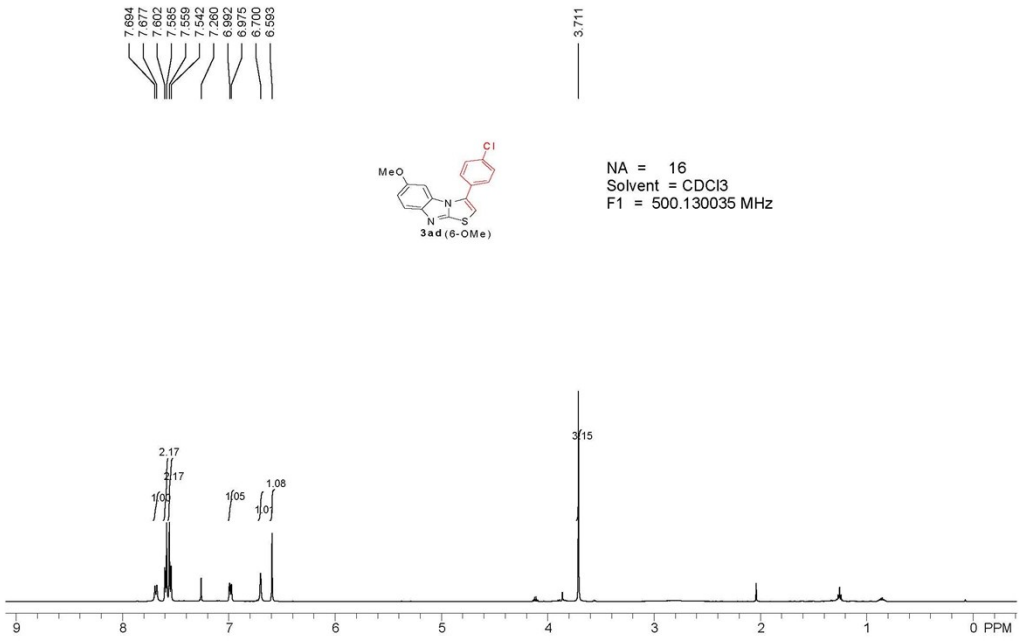


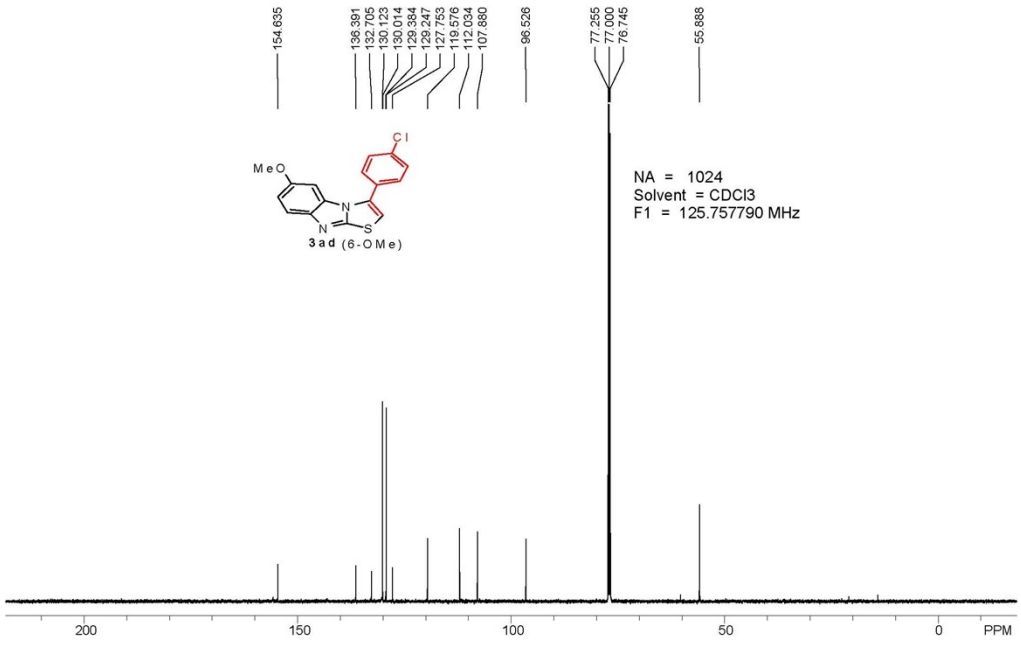
3-(4-Chlorophenyl)-6-nitro-thiazolo[3,2-a]benzimidazole (3ac)



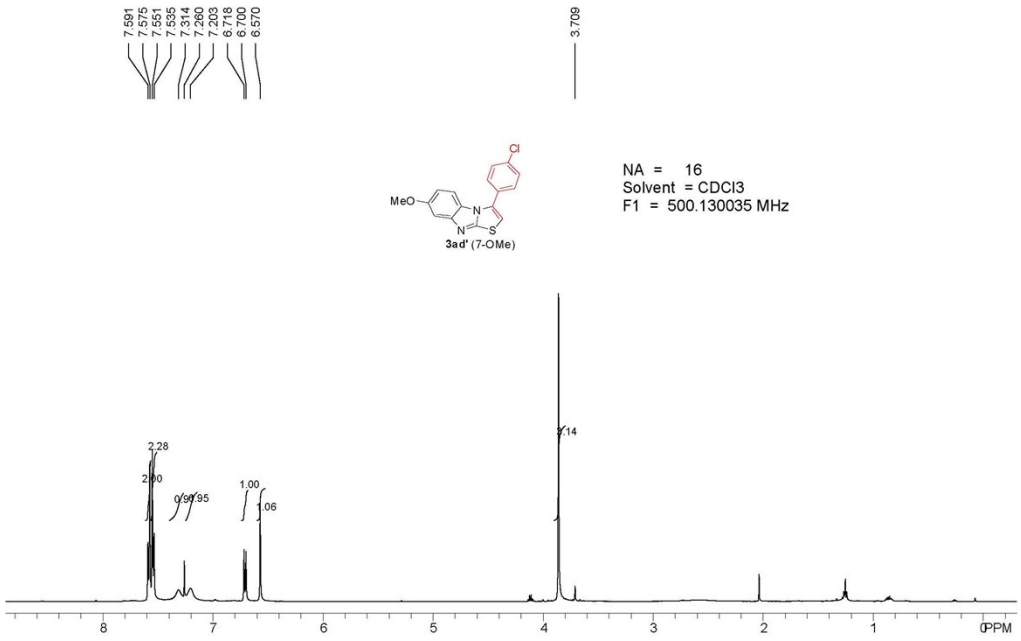


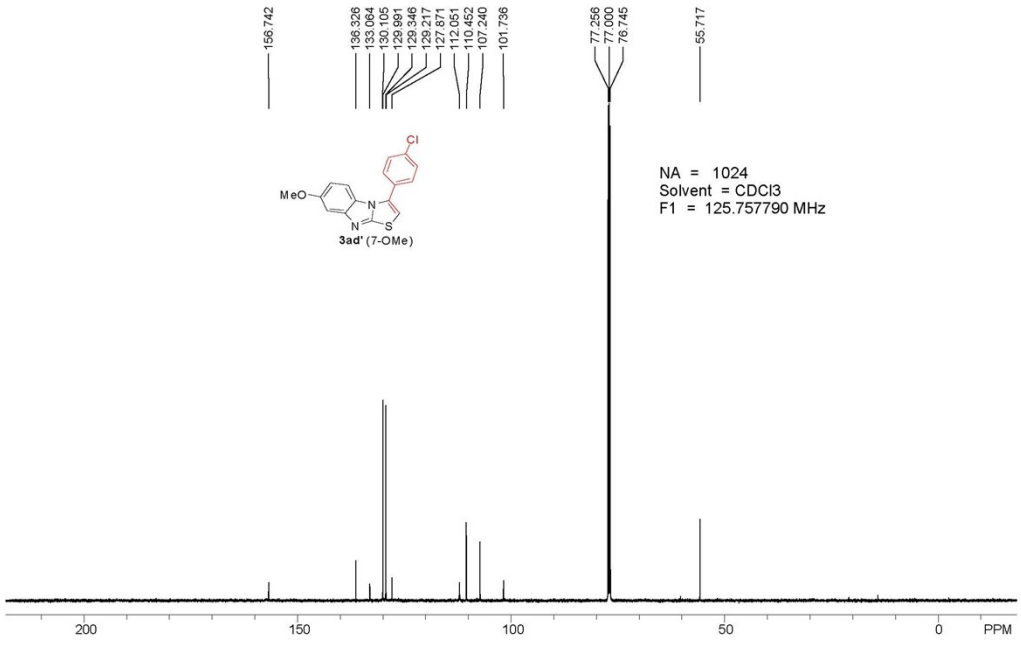
3-(4-Chlorophenyl)-6-methoxy-thiazolo [3,2-a] benzimidazole (3ad)



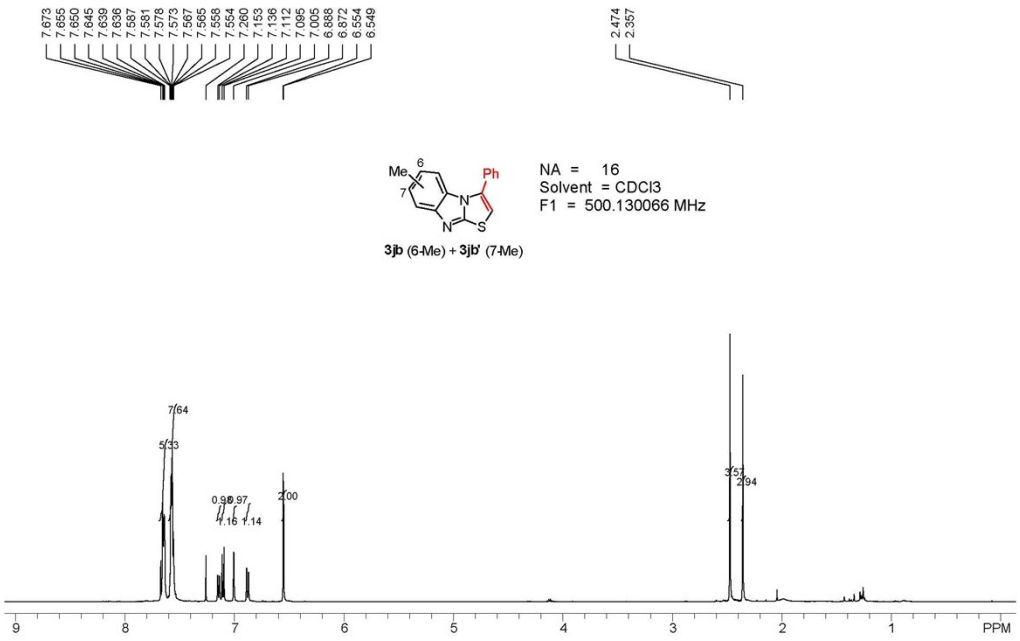


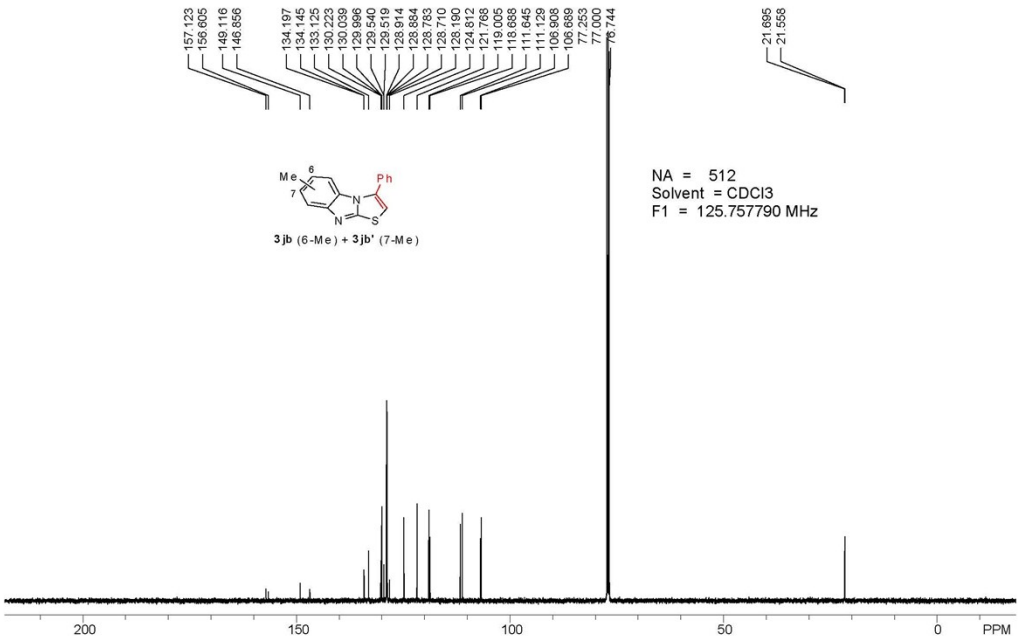
3-(4-Chlorophenyl)-7-methoxy-thiazolo[3,2-a]benzimidazole (3ad')



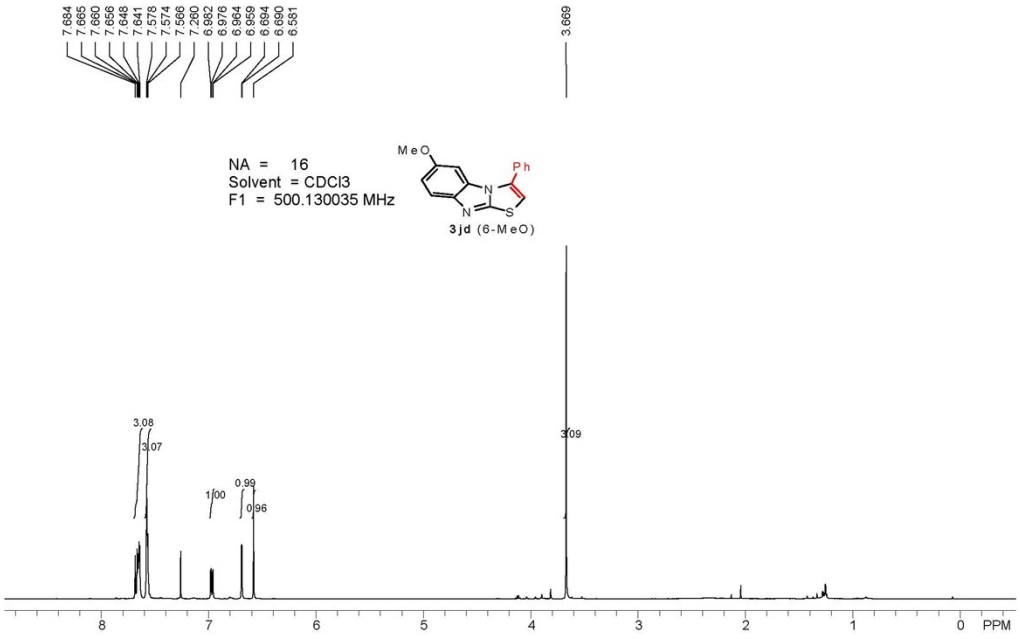


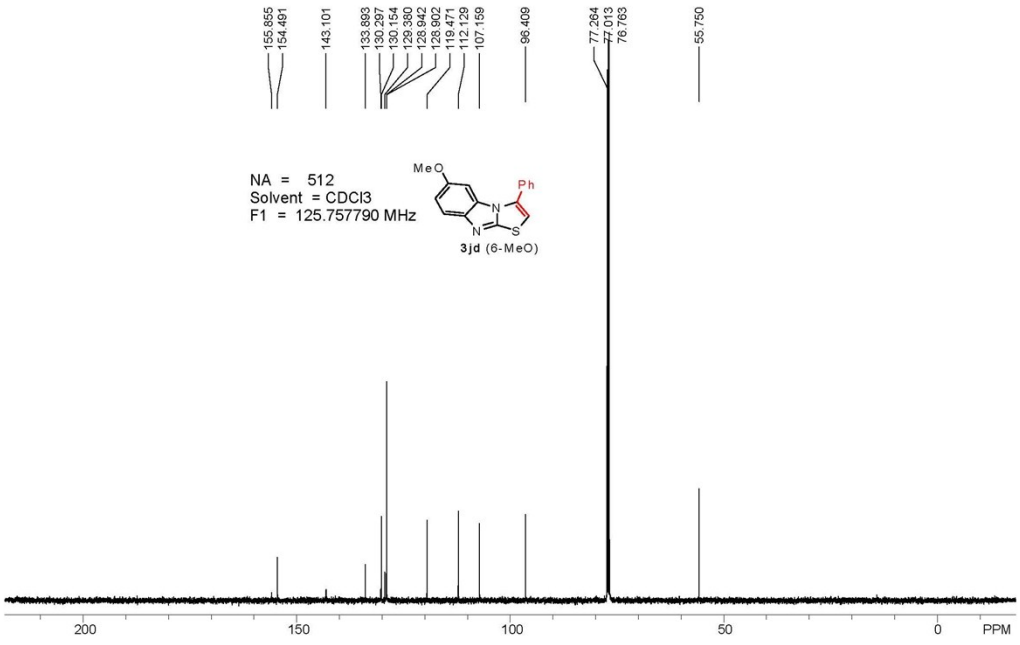
3-(4-Chlorophenyl)-6-methyl-thiazolo[3,2-a]benzimidazole (3jb) and 3-(4-Chlorophenyl)-7-methyl-thiazolo[3,2-a]benzimidazole (3jb')



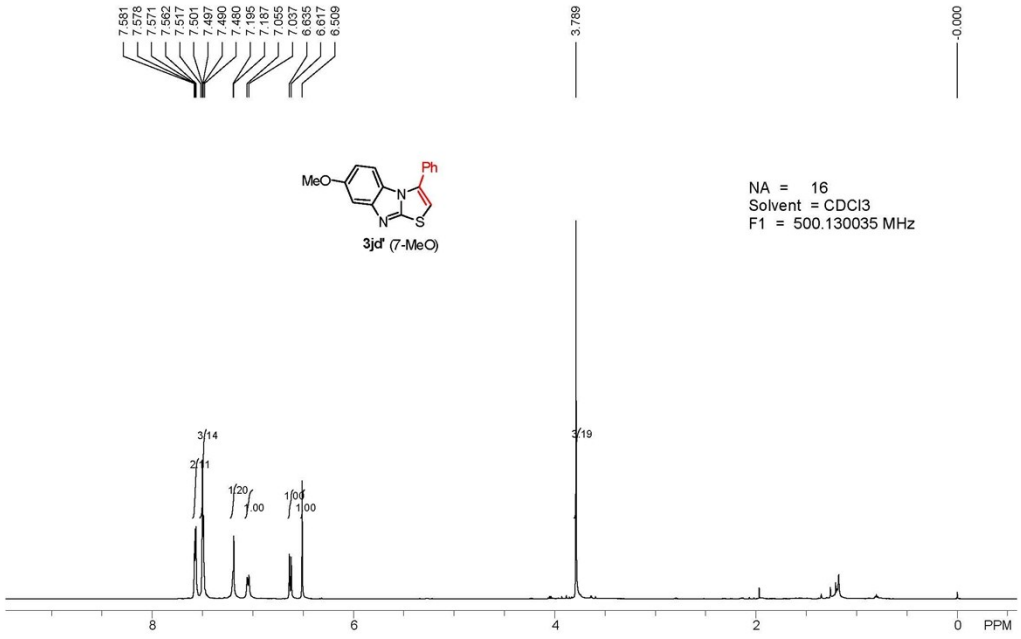


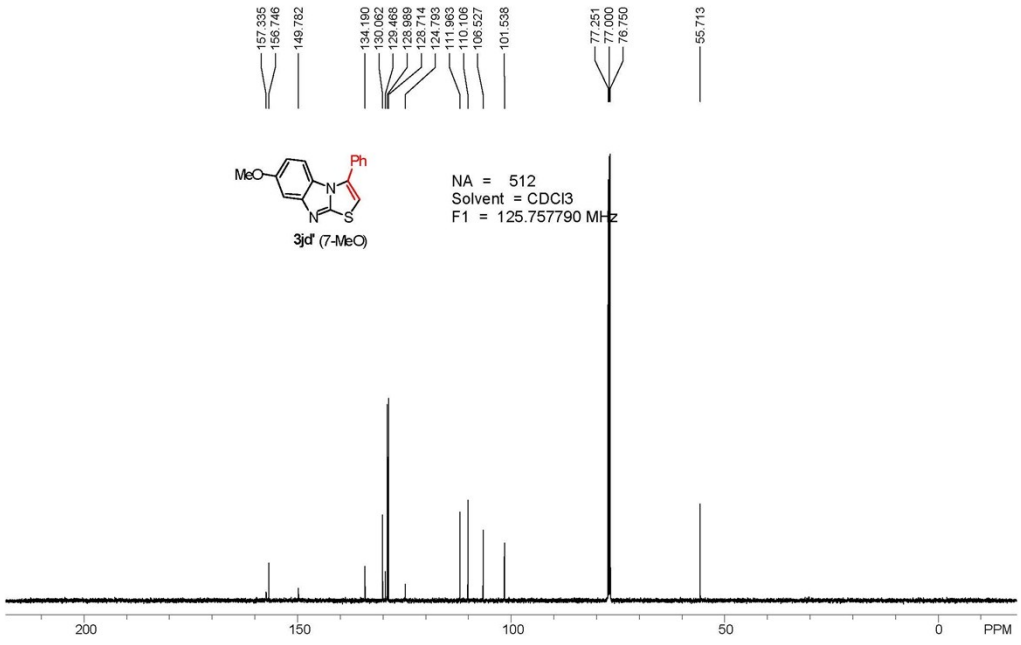
3-Phenyl-6-methoxy-thiazolo[3,2-a]benzimidazole (3jd)



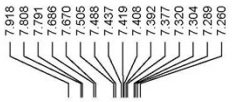


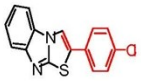
3-phenyl-7-methoxy-thiazolo[3,2-a]benzimidazole (3jd')





2-(4-Chlorophenyl)thiazolo[3, 2-a]benzimidazole (4aa)





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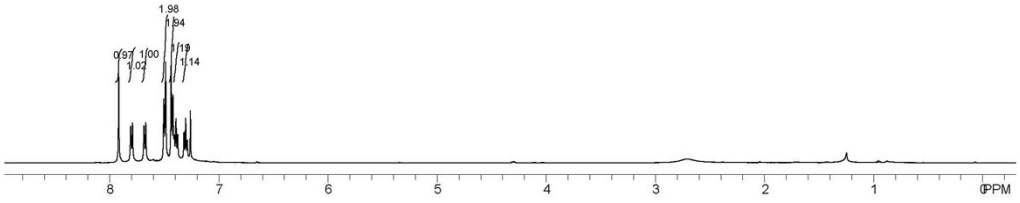
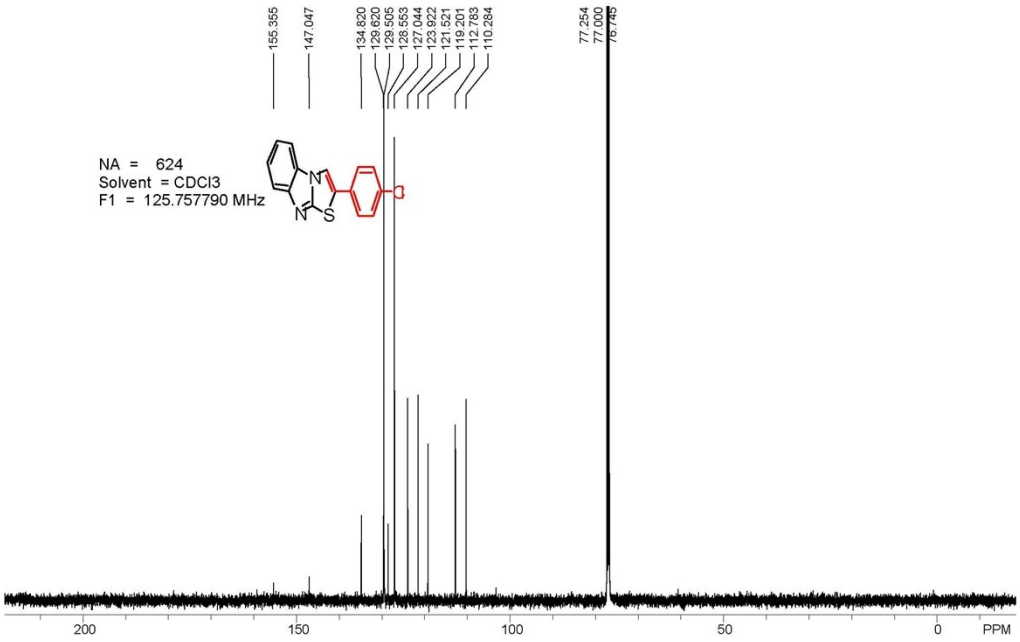
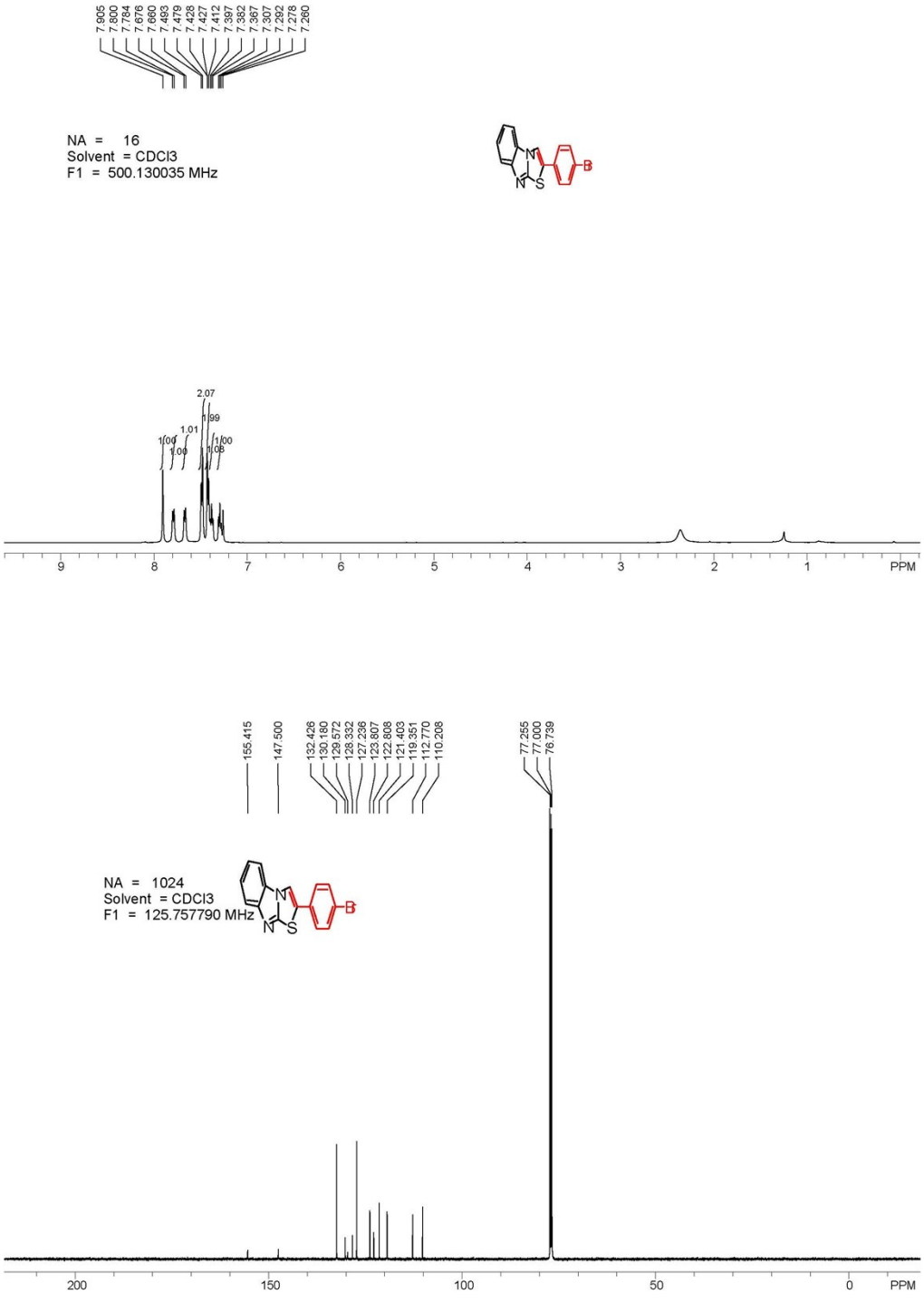
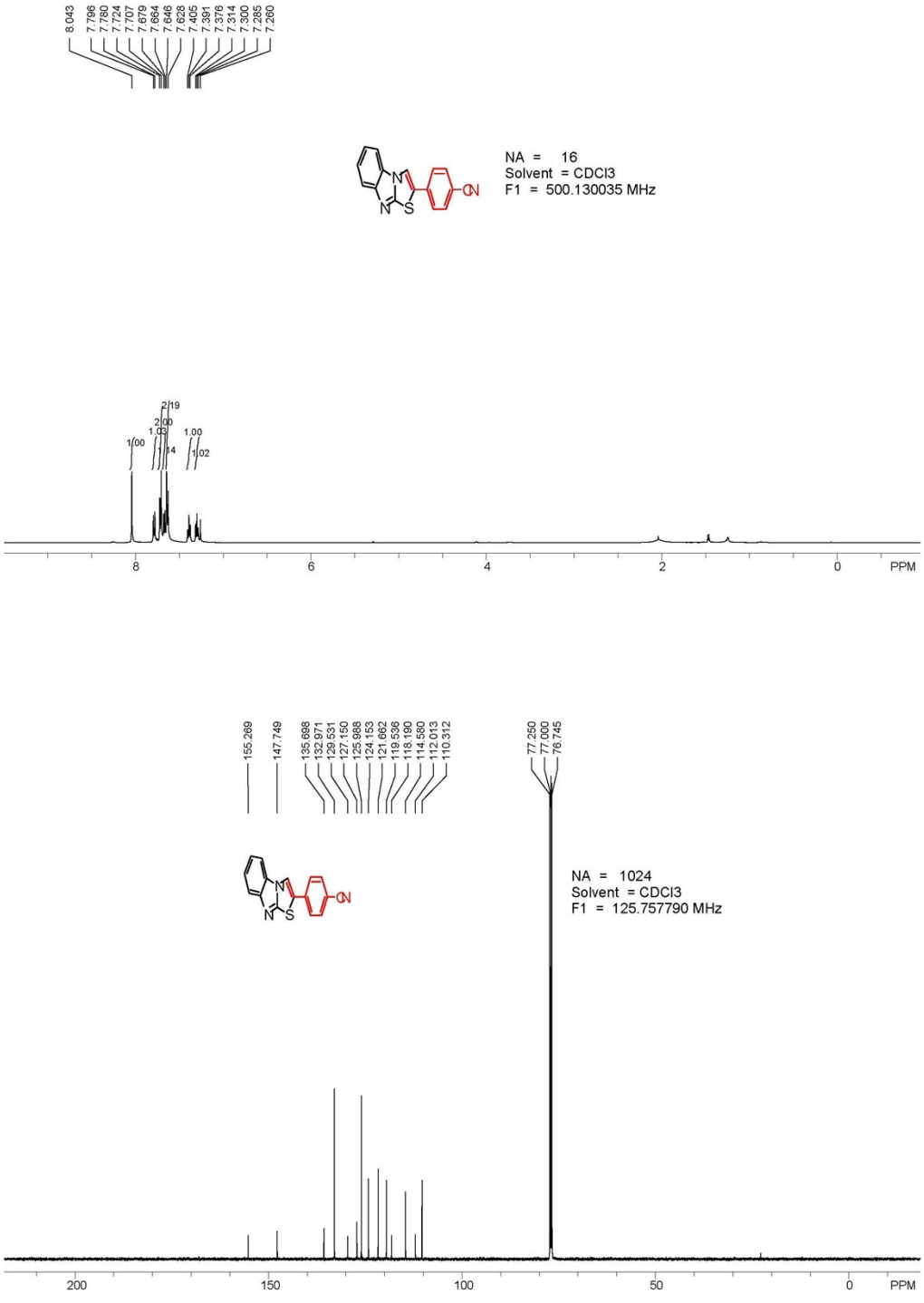




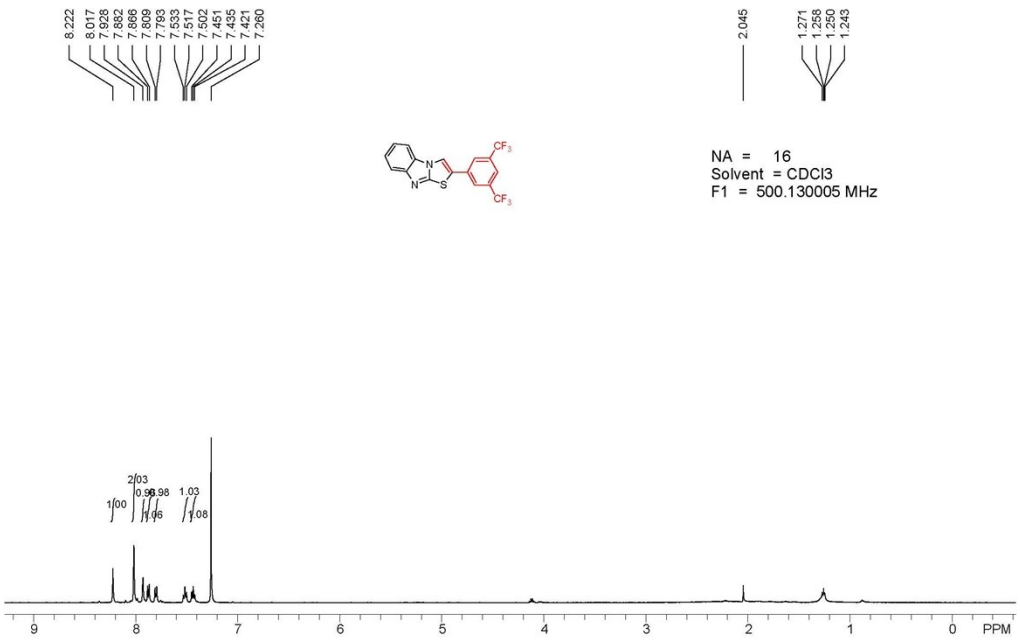
2-(4-Bromophenyl)thiazolo[3, 2-a]benzimidazole (4ba)

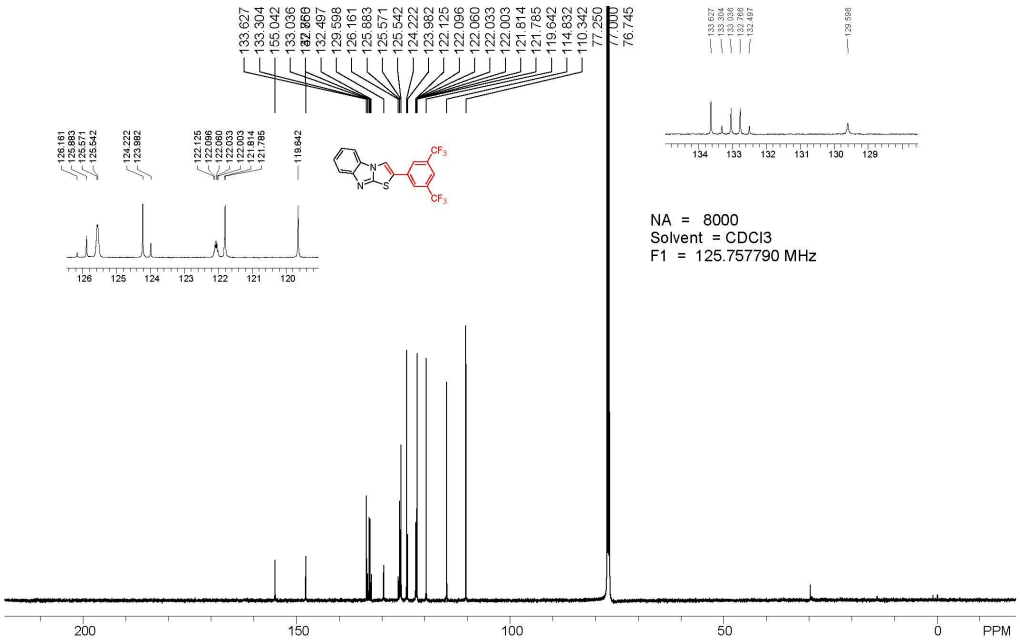


2-(4-Cyanophenyl)thiazolo[3, 2-a]benzimidazole (4da)

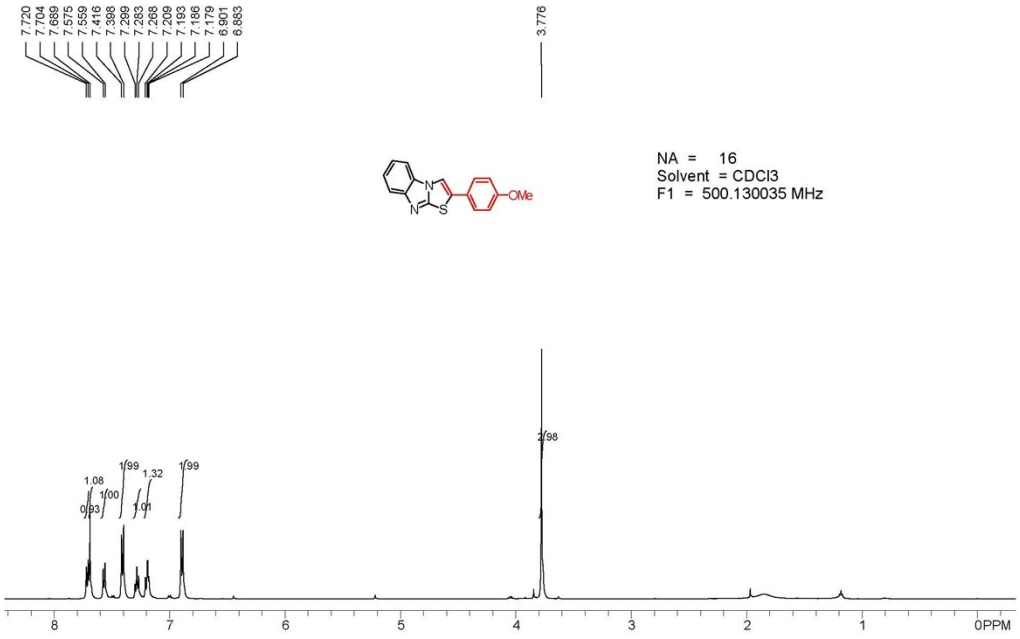


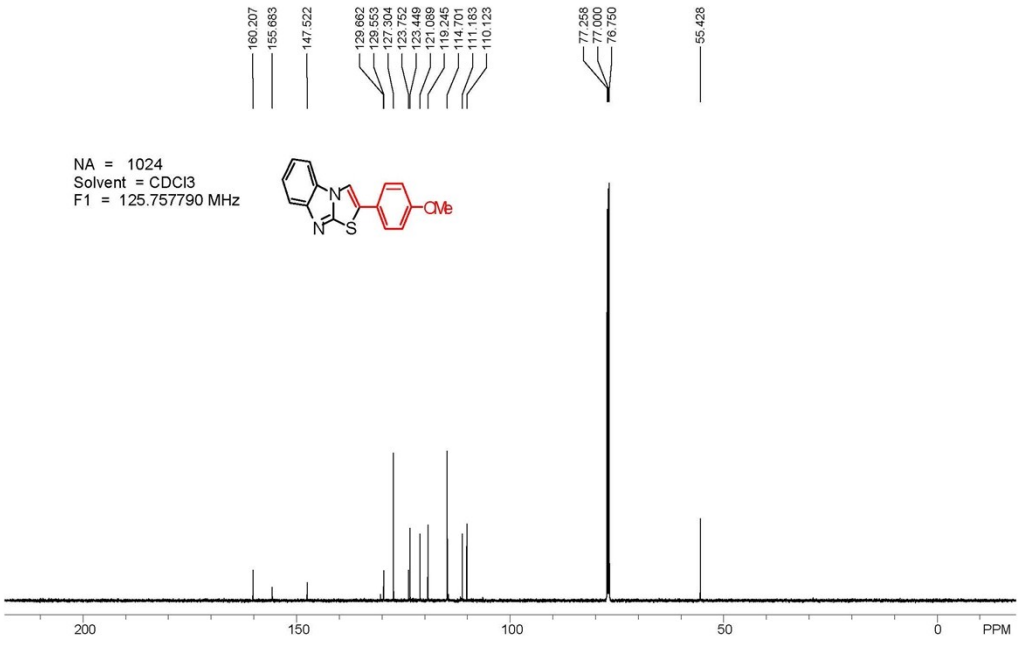
2-(3,5-bis(trifluoromethyl)phenyl)thiazolo[3, 2-a]benzimidazole (4ka)



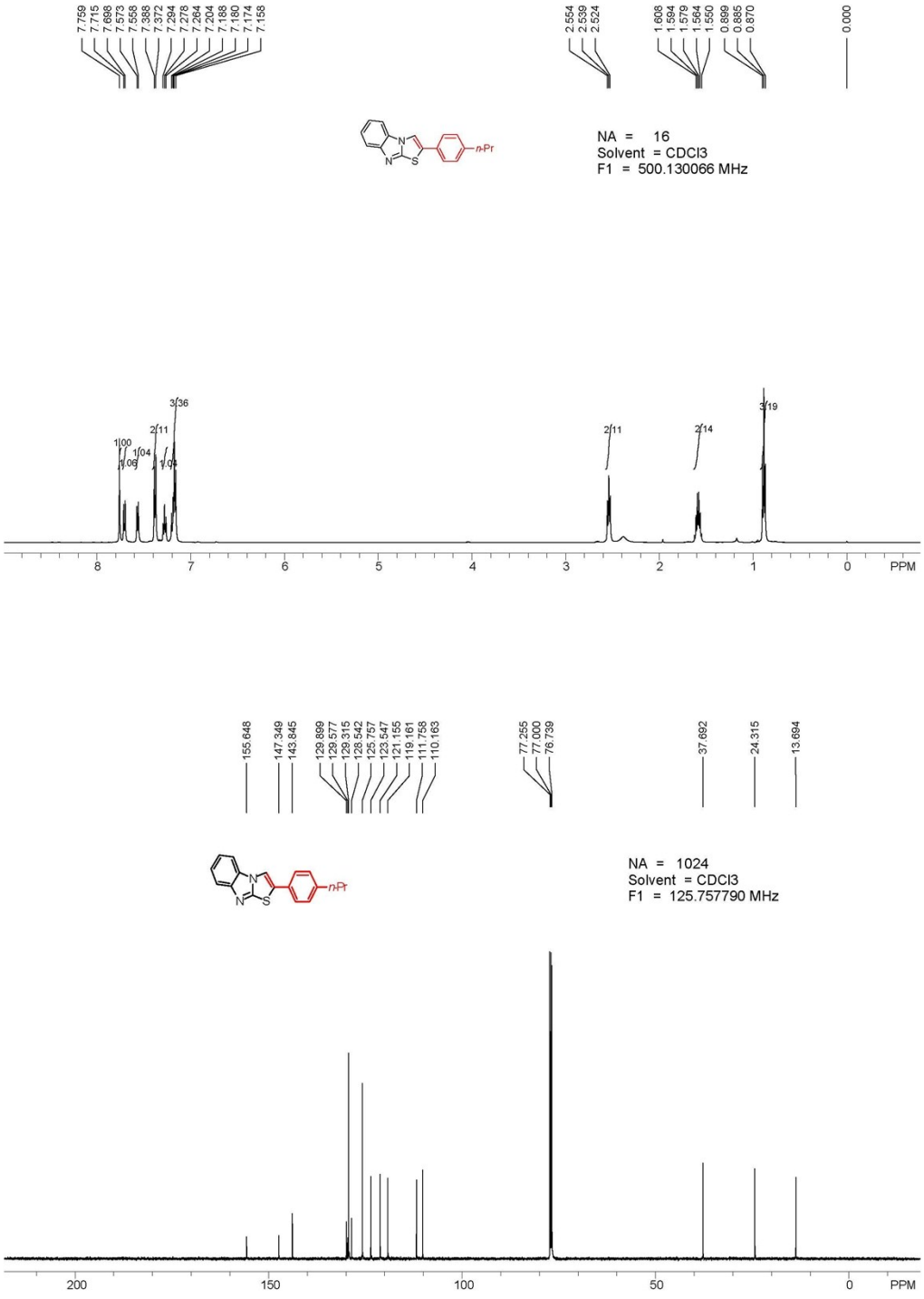


2-(4-Methoxyphenyl)thiazolo[3, 2-a]benzimidazole (4ga)

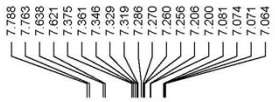


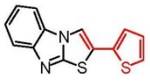


2-(4-Propylphenyl)thiazolo[3, 2-a]benzimidazole (4ha)

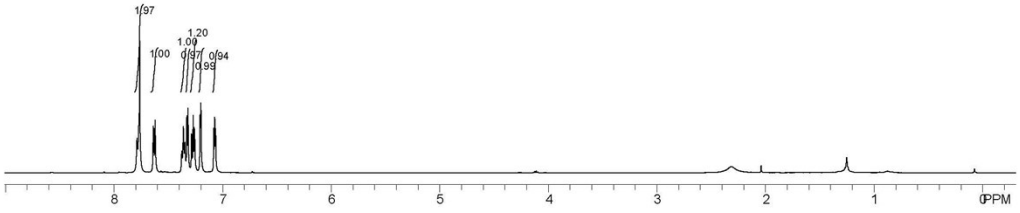


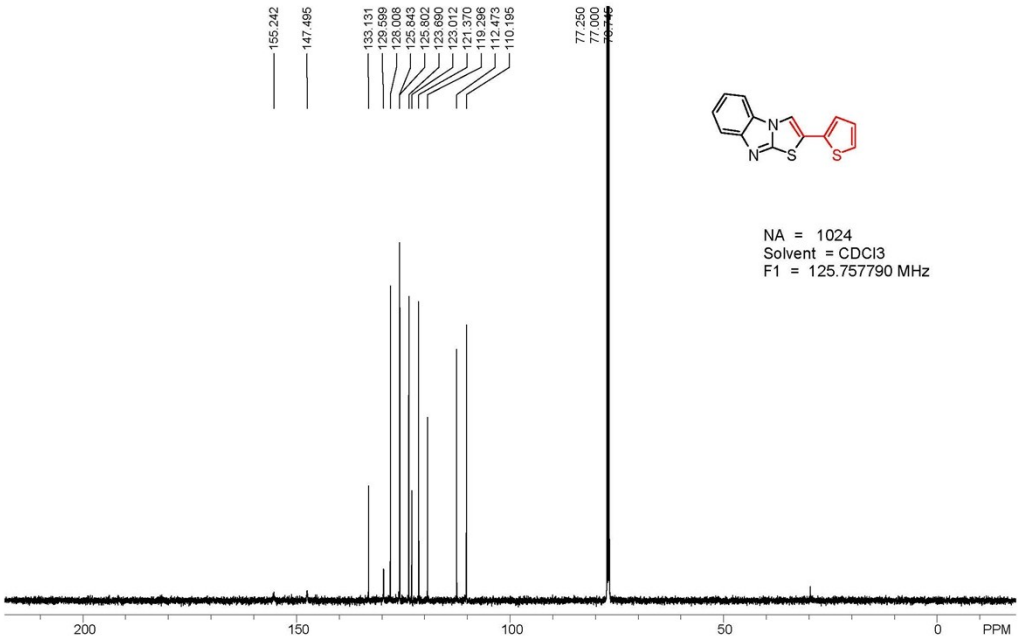
2-Thiophen-2-ylthiazolo[3,2-a]benzimidazole (4la)





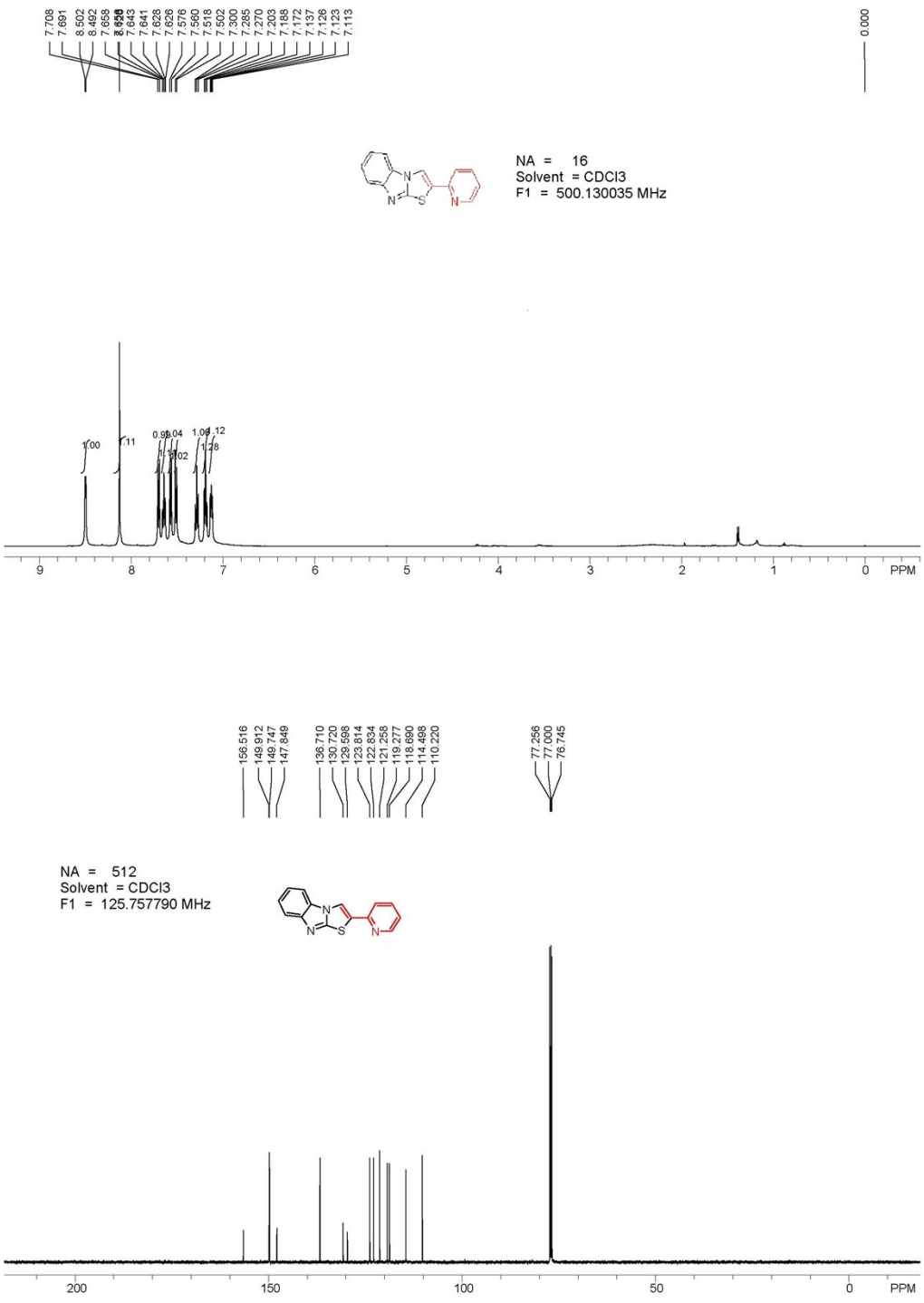
NA = 16
Solvent = CDCl3
F1 = 500.130066 MHz



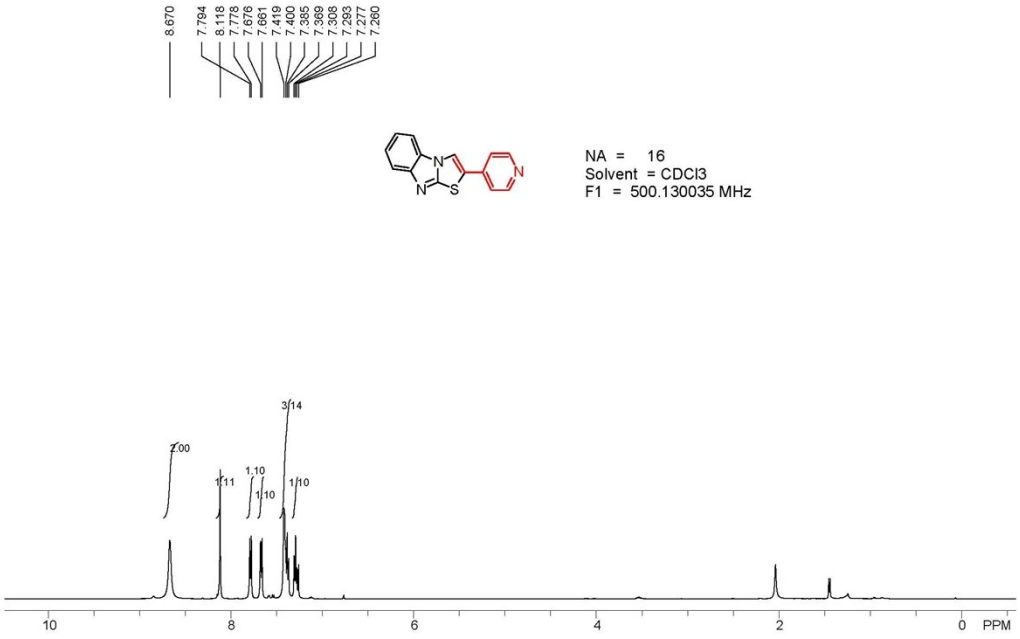


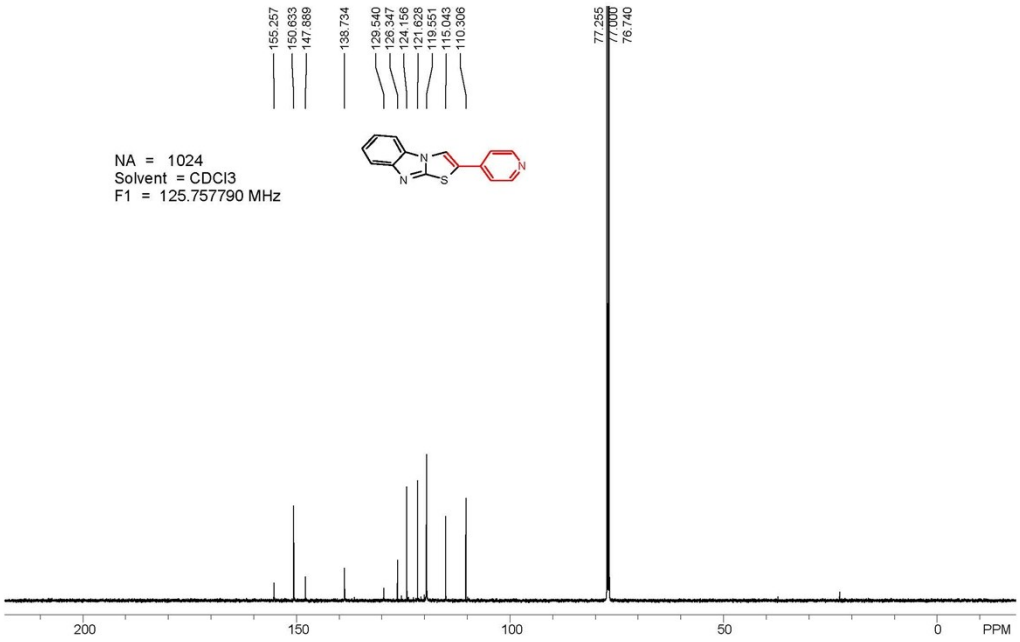
NA = 1024
Solvent = CDCl3
F1 = 125.757790 MHz

2-Pyridin-2-ylthiazolo[3,2-a]benzimidazole (4na)

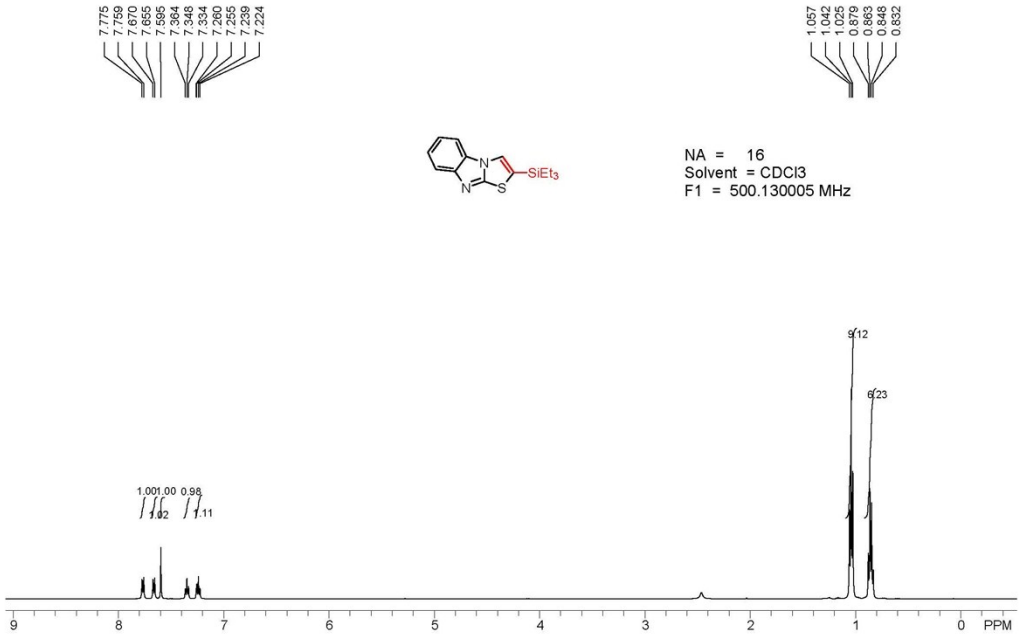


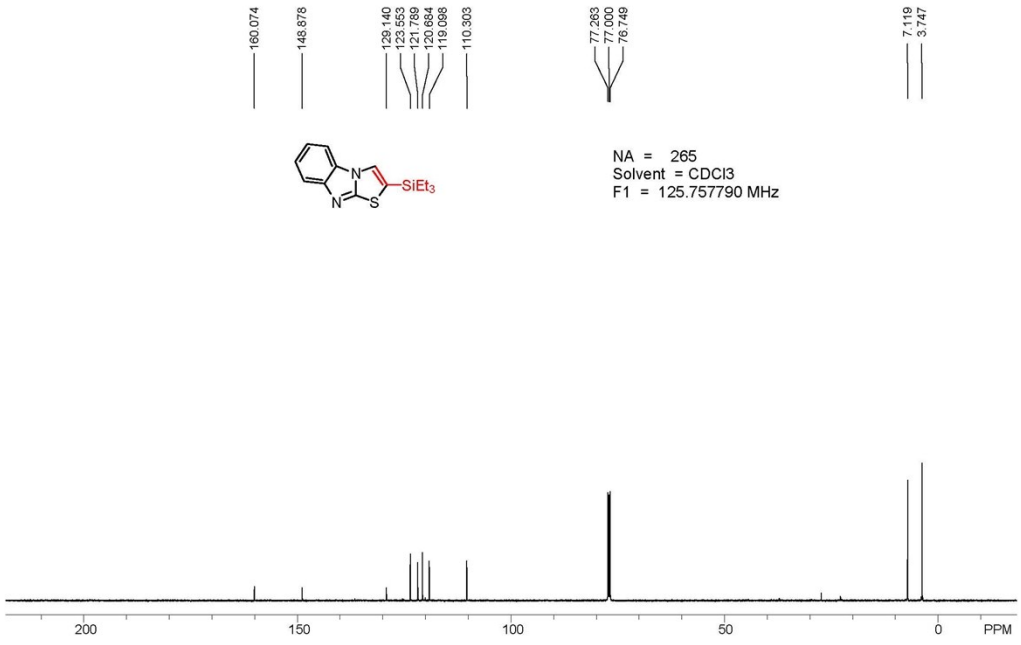
2-Pyridin-4-ylthiazolo[3,2-a]benzimidazole (4oa)



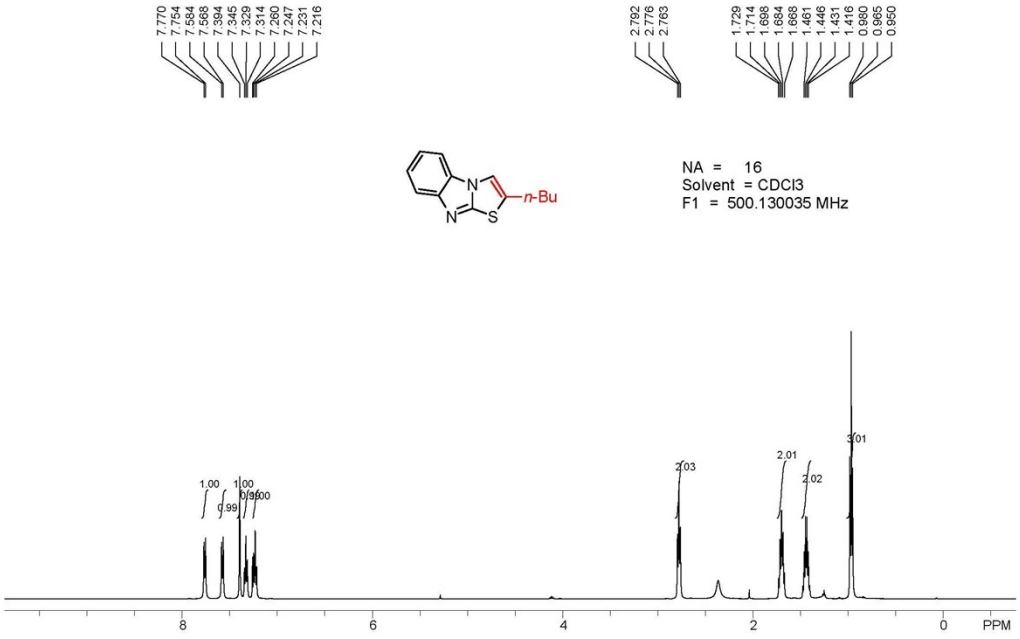


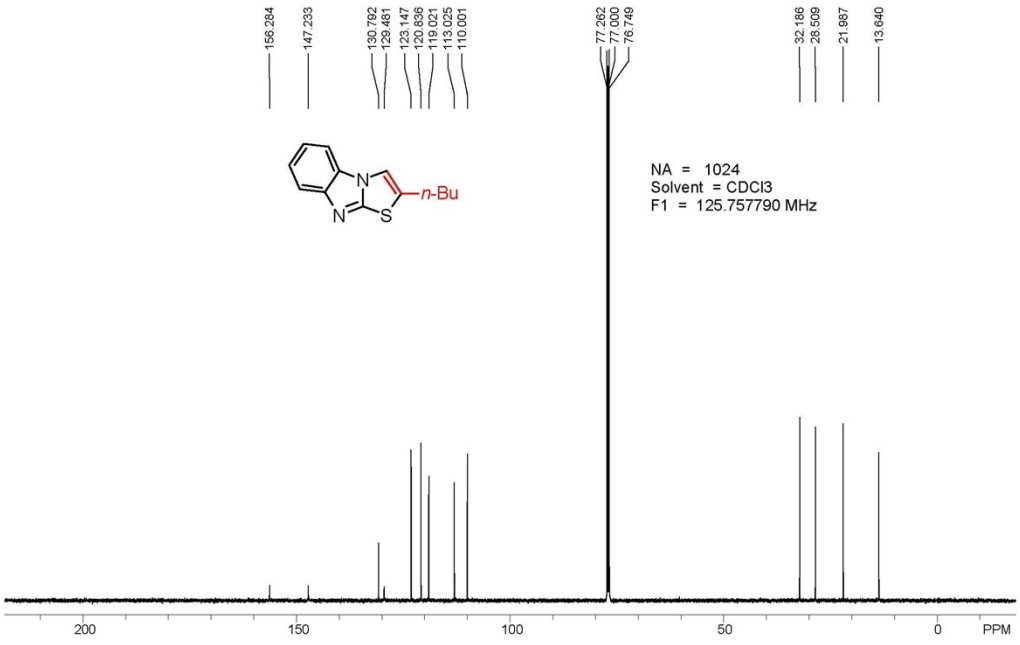
2-(Triethylsilyl)thiazolo[3,2-a]benzimidazole (4qa)



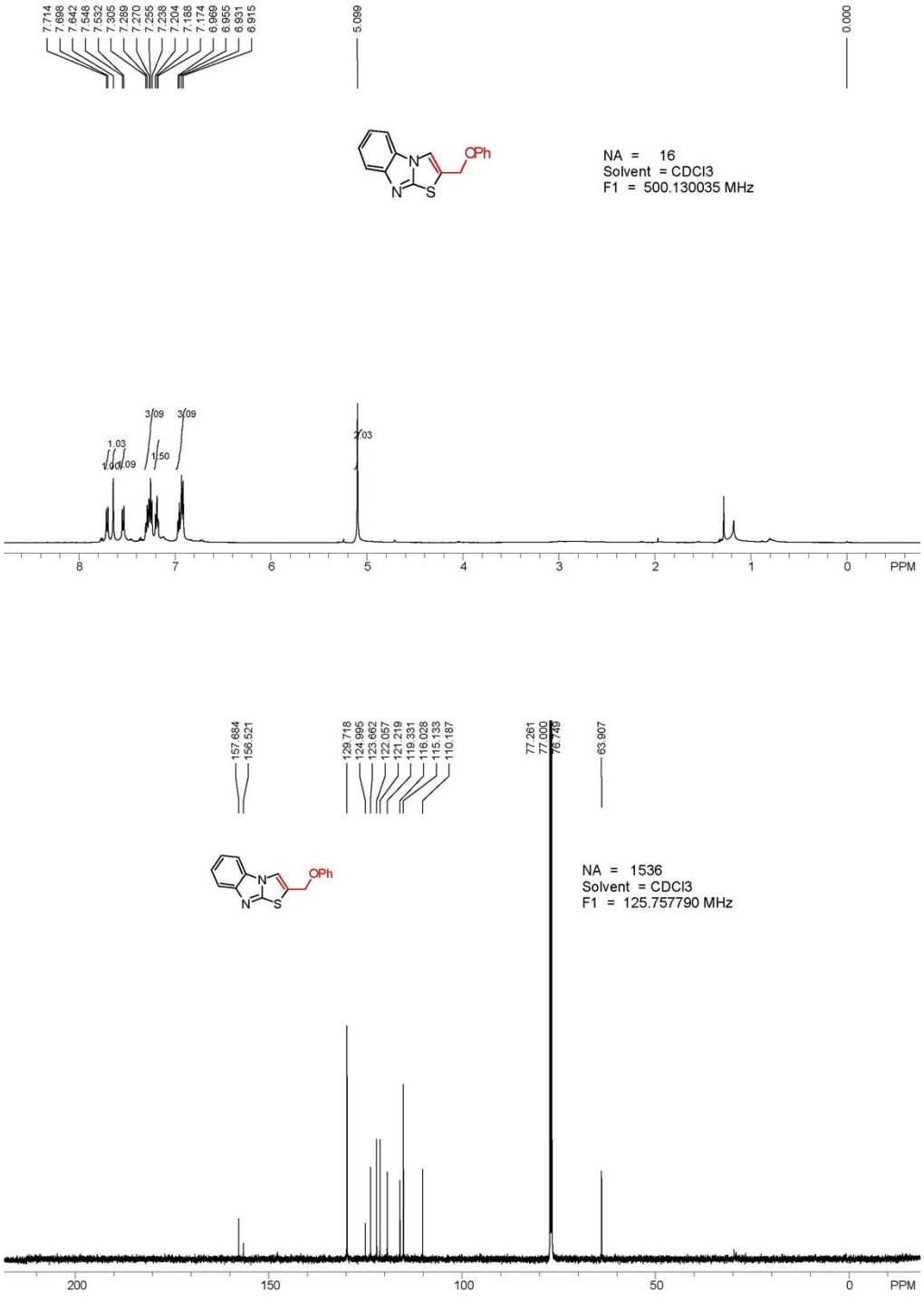


2-Butylthiazolo[3,2-a]benzimidazole (4ua)

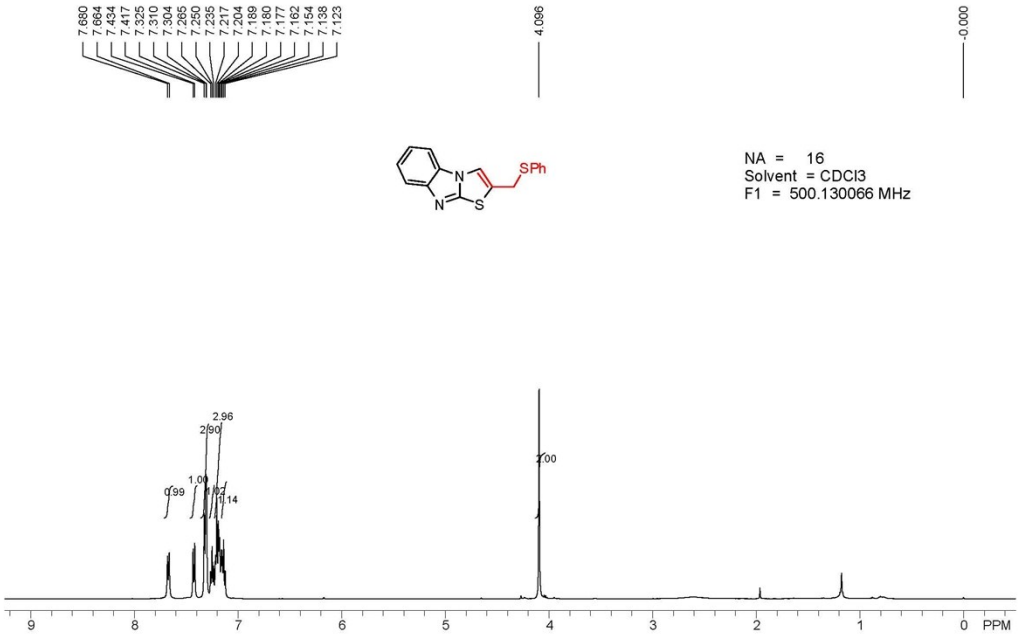


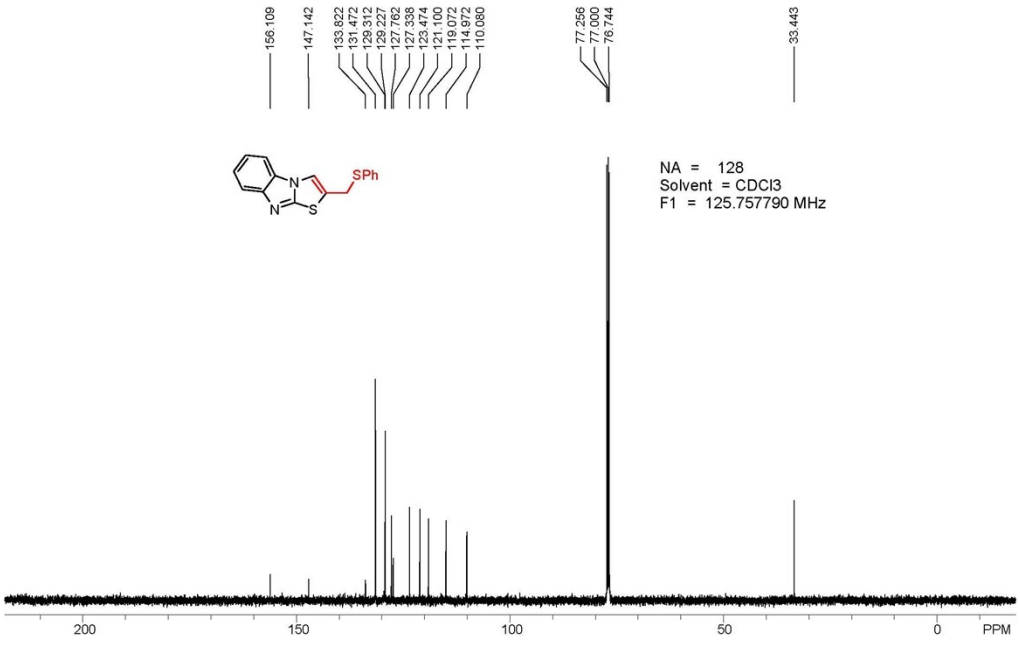


2-Phenoxymethylthiazolo[3,2-a]benzimidazole (4xa)

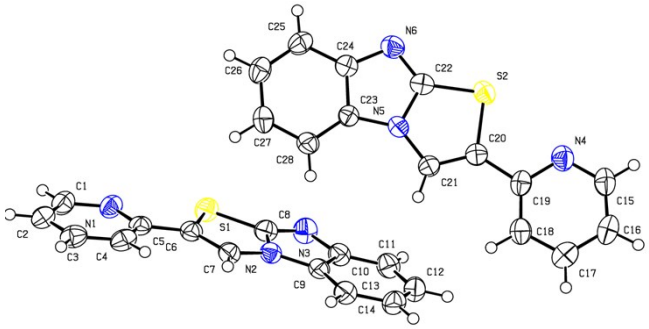


2-Phenylthiomethylthiazolo[3,2-a]benzimidazole (4ya)





Crystal data and structure refinement for **4na**



CCDC Number	1847875
Empirical formula	C14 H9 N3 S
Formula weight	251.30
Crystal size, mm^3	0.05 × 0.04× 0.03
Temperature, *T*	298(2) K
Wavelength, *λ* (Å)	0.71073
Crystal system	Orthorhombic
Space group	P c a 21
Unit cell dimensions	*a* = 22.656(3) Å *b* = 5.7765(7) Å *c* = 17.163(2) Å *α* = 90°, *γ* =90°, *β* = 90°
Volume, *V* ($Å^3$)	2246.2(5)
Z	8
Calculated density, $Mg·m^{-3}$	1.486
Absorption coefficient, *μ* (mm^{-1})	0.270
F(000)	1040
θ range for data collection	1.80° to 25.50°
Limiting indices	–27 ≤ *h* ≤ 27, –6 ≤ *k* ≤ 6, –20 ≤ *l* ≤ 20
Reflection collected/unique	18087 / 4147 [R(int) = 0.0413]
Completeness to *θ* = 25.50	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9607 and 0.9381
Refinement method	' SHELXL-2016/6 ' Full-matrix least-squares on F^2
Data/restraints/parameters	4147 / 1 / 326
Goodness–of–fit on F^2	1.090
Final *R* indices [*I*>2sigma(*I*)]	R1 = 0.0366, wR2 = 0.0976
R indices (all data)	R1 = 0.0380, wR2 = 0.0988
Largest diff. peak and hole	0.304 and -0.308 $e·Å^{-3}$
Absolute structure parameter	0.14(7)
Extinction coefficient	0.0145(14)